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Characterization of magnesium promoted Co/SiO_2 catalysts

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Co/SiO_2, Mg–Co/SiO_2, and Co–Mg/SiO_2 catalysts were prepared from nitrate precursors to get more insight into the effect of magnesium promotion on the cobalt catalyst. The desorption characteristics and reactivity of the catalysts towards synthesis gas were evaluated in a pulse micro reactor connected to an on-line quadrupole mass spectrometer. The presence of MgO both decreased the extent of reduction and increased the dispersion of cobalt. The reactivity results suggested that MgO promotion created new types of active sites, probably at the edge sites of cobalt and magnesium. The highest activity per metallic site available was obtained with a Mg : Co molar ratio of 1/2, i.e. with a high amount of edge sites. In accordance with previous results the formation of CO_2 was clearly suppressed in the presence of MgO, and methanol was formed in trace amounts.

Keywords: catalyst characterization; cobalt; magnesium; silica support; carbon monoxide hydrogenation; synthesis gas; Fischer–Tropsch

1. Introduction

Cobalt and magnesium, classically used as Fischer–Tropsch catalysts [1,2], have also received attention as model systems. Surface studies of cobalt foil model catalysts have indicated that the addition of metallic magnesium (Mg) increases the capacity for CO adsorption [3], whereas both metallic and partially oxidized MgO_x ($x = 0.5$) promote the dissociation of CO [3–5]. However, on supported, partially reduced cobalt catalysts, magnesium is present as MgO rather than as partially oxidized MgO_x or Mg. Studies on cobalt foil model catalysts promoted with MgO have shown MgO to decrease the adsorption capacity of CO and to hinder dissociation [4,5].

MgO finds use in heterogeneous catalysis both as a promotor and as a support. On supported cobalt catalysts, MgO promotion decreases the extent of reduction [1,6–8] and thus reduces the amount of active metallic cobalt sites on the surface. MgO also facilitates the formation of formate species by the reaction of CO and

H_2O [9,10]. The formate species may subsequently be hydrogenated to yield methane [11] or methanol, or decomposed to give CO and H_2O [9] or CO_2 and H_2 [10]. In fact, it has been proposed that most of the CO_2 formed on Rh/MgO arises from the reaction $CO(m) + OH(s) \rightarrow COOH(s) \rightarrow CO_2 + \frac{1}{2}H_2$ (where (s) refers to the support and (m) to the Rh metal) [12]. On Co/MgO, chemisorption of CO results in the formation of $Co(CO)_4^-$ and CO_3^{2-} species at the periphery of the cobalt particles [13]. Hence, some of the CO_2 formation may be attributed to the decomposition and/or desorption of these carbonyl and carbonate species [12].

Our previous results [6] have indicated that the effect of MgO promotion on nitrate derived catalysts is dependent on the surface morphology. The activity of Mg–Co/SiO_2 catalysts is lower than that of Co/SiO_2, and the formation of CO_2 is decreased in the case of promotion. The activity of Co–Mg/SiO_2 is similar to that of the unpromoted catalyst, whereas the probability of chain growth and the yield of CO_2 are lower. The reduction in the CO_2 production of all the promoted catalysts was probably caused by modification of the active sites due to the presence of MgO [4,9,13]. The present study was performed to get more insight into the surface characteristics of magnesium promoted catalysts. The aim was to determine the effects of the interaction of the magnesium and cobalt species on the activity and selectivity of the catalysts.

2. Experimental

2.1. CATALYSTS

The following nomenclature has been used: 2-Co–Mg/SiO_2 refers to a catalyst first impregnated with magnesium nitrate and then with cobalt nitrate. The number in front refers to the molar ratio of Mg : Co on the support. The catalyst preparation has been described in detail in a previous publication [6]. The impregnated catalysts were calcined at 300°C (3°C/min) under 3 ℓ/h air flow for 12 h to enhance their reducibility [14]. The catalysts were reduced in situ at 450°C prior to the reaction studies. The metal contents of the catalysts are shown in table 1. The dispersions of the catalysts reduced at 450°C were determined by standard static chemisorption measurements. Standard experimental procedures [15,16] were utilized, and the results are based on the total hydrogen uptake at 25°C. The dispersions and the estimates of particle size estimates assuming spherical geometry of uniform size were corrected with the extents of reduction.

2.2. REACTIVITY

The temperature programmed studies and the pulse reaction studies were carried out in a down flow quartz tubular microreactor connected to a Balzers quadrupole mass spectrometer. A catalyst sample of 300 mg was reduced in situ at 450°C for

Table 1
The Co and Mg contents of the prepared catalysts (AAS determinations)

Metal	Co/SiO_2	1/2[a]-Mg–Co/SiO_2[b]	2[a]-Mg–Co/SiO_2[b]	2[a]-Co–Mg/SiO_2[c]
Co wt%	5.06	4.70	4.44	4.46
Mg wt%		0.96	3.58	3.53

[a] Mg : Co molar ratio.
[b] Carrier impregnated with cobalt solution, dried and impregnated with magnesium solution.
[c] Carrier impregnated with magnesium solution, dried and impregnated with cobalt solution.

2 h under 100 ml/min flow of 3% H_2 in Ar (H_2-Ar). The catalyst was cooled to 25°C, the carrier was switched to He flow of 60 ml/min, and the catalyst was pulsed with 10 pulses (0.5 ml) of H_2. Thereafter the temperature was raised from 25 to 450°C at a rate of 20°C/min under He flow of 60 ml/min (TPD). The H_2 pulses were repeated, now at 250°C, and the TPD was carried out from 250 to 450°C. The CO pulsing at 25°C and subsequent TPD were carried out as for H_2. After the TPD the carbonaceous residues were removed from the surface by cooling the sample to room temperature and then elevating the temperature again, from 25 to 450°C, under H_2-Ar flow of 60 ml/min (TPSR). Thereafter the catalyst was subjected to 10 pulses of CO at 25°C under H_2-Ar flow of 60 ml/min to estimate the initial reactivity. After the TPD, the CO pulsing was repeated at 250°C under H_2-Ar, with subsequent TPD from 250 to 450°C.

The steady-state reactivity studies were carried out in the automated down flow tubular reactor described in our previous publication [6]. The reactions were carried out at 235–290°C, 0.5 MPa with 3 : 1 : 3 molar ratio of Ar : CO : H_2. The amount of catalyst used was 1 g.

3. Results and discussion

3.1. CHARACTERIZATION OF THE CATALYSTS

The catalysts were characterized by XRD [6], XPS and chemisorption determinations (see table 2). In agreement with previous results [1,6–8] magnesium promotion reduced the extent of reduction. Despite the lower extent of reduction, the hydrogen uptakes of 2-Mg–Co/SiO_2 and 2-Co–Mg/SiO_2 in the static chemisorption were higher than the hydrogen uptake of Co/SiO_2.

The dispersions corrected with the extent of reduction were 5.5 and 5.1% for Co/SiO_2 and 1/2-Mg–Co/SiO_2, and 12 and 9.7% for 2-Mg–Co/SiO_2 and 2-Co–Mg/SiO_2. The values for particle sizes obtained by chemisorption correlated well with previous XRD determinations [6]. The results indicate that MgO promotion with a Mg : Co molar ratio of 2 decreased the particle size of cobalt, i.e. increased the dispersion. The dispersions were lower than those obtained by Reuel and

Table 2
The characteristics of the Co/ SiO$_2$ catalysts after reduction with hydrogen at 450°C

Catalyst on SiO$_2$	H_2 uptake (μmol/g_{cat})	Dispersion (%)	Reduction XPS (%)	Dispersion[c] (%)	Size (nm)		Mg/CO (mol/mol)	
					XRD	chemisorption	AAS	XPS
Co	12.36	3.0	54	5.5	14	17	0	0
1/2-Mg–Co[a]	10.96	2.8	55	5.1	10	19	0.5	0.6
2-Mg–Co[a]	15.9	4.2	35	12.0	11	8	2.0	3.8
2-Co–Mg[b]	14.92	4.0	41	9.7	10	10	1.9	1.4

[a] Carrier impregnated with cobalt solution, dried and impregnated with magnesium solution.
[b] Carrier impregnated with magnesium solution, dried and impregnated with cobalt solution.
[c] Dispersion corrected with the extent of reduction.

Bartholomew [17] for Co/SiO_2 and Wiswanathan and Gopalakrishnan [18] for Co/KG, but similar to the values of Hoff [16] for nitrate derived catalysts.

3.2. PULSE REACTOR STUDIES

3.2.1. Hydrogen adsorption and desorption

In the pulse flow reactor the reduced catalyst sample was flushed with He, and pulsed thereafter with hydrogen at 25°C. The adsorption capacity of the samples was too low to permit the detection of hydrogen adsorption during hydrogen pulsing. The hydrogen pulses were accompanied by small background pulses of water (moisture). TPD was carried out to remove any adsorbed species from the surfaces.

According to the TPD results the water evolution was greater for all MgO promoted catalyst samples than for Co/SiO_2. The water formation could hardly have been due to reduction since the catalysts had already been reduced at 450°C. More likely, MgO retained moisture through hydroxide formation [19,20], and this water was released during the TPD. The increased ability of MgO promoted catalysts to retain and release water was also observed during the hydrogen pulses at 250°C and subsequent TPD.

3.2.2. CO adsorption and desorption

CO pulses introduced to the catalysts at 25°C resulted in the evolution of hydrogen, methane, CO, and CO_2. Apparently, the hydrogen was replaced by CO, CO dissociated and the surface carbon thus formed reacted to either CO_2 or methane. The intensity of methane formation was about the same for all catalysts, whereas the intensity of CO_2 formation decreased with increasing amount of MgO. The catalysts with Mg : Co atomic ratio of 2 produced almost no CO_2.

The adsorbed species retained on the catalyst surfaces during CO pulsing were removed by subsequent TPD. Desorption of CO, CO_2, and water was observed with all samples. The presence of MgO significantly altered the desorption of CO, as shown in fig. 1. The intensity of the first desorption peak of CO was increased by MgO addition and the increase was greater with a Mg/Co ratio of 1/2 than with a ratio of 2. The second CO desorption peak was shifted to higher temperature by MgO promotion, and the intensity was enhanced by Mg : Co ratio of 1/2. Thus MgO increased the CO adsorption capacity considerably for a Mg : Co atomic ratio of 1/2 and slightly for an atomic ratio of 2. In a study of Mg promoted model surfaces Vaari et al. [3] observed that as the surface coverage of Mg increased above 0.4, the neighboring Mg islands began to merge. On this basis we suggest that the edge sites of MgO and cobalt were greatest in number with a Mg : Co atomic ratio of 1/2, and that the CO adsorption on the edge sites probably resulted in the formation of $Co(CO)_4^-$ and CO_3^{2-} species [13]. In the case of 2-Mg–Co/SiO_2 and 2-Co–Mg/SiO_2, the order of impregnation had no significant influence on the desorption, and in both cases MgO probably blocked some of the cobalt CO adsorption sites, as observed in the model surface studies [4,5] and with MgO promoted catalysts [1].

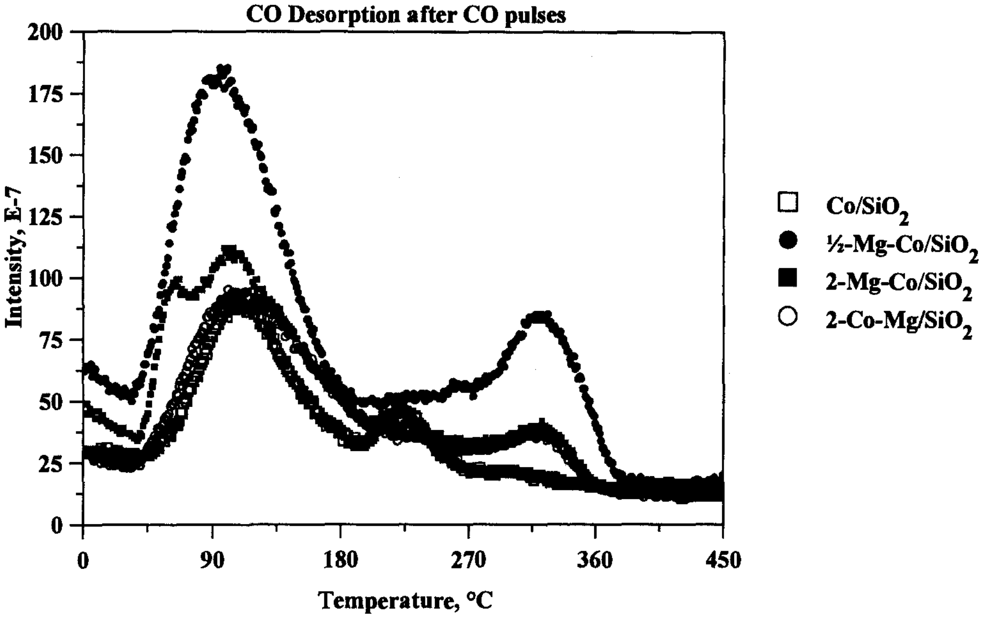

Fig. 1. CO desorption from Co/SiO_2, 1/2-Mg–Co/SiO_2, 2-Mg–Co/SiO_2 and 2-Co–Mg/SiO_2 after CO pulses at 25°C.

The sites responsible for CO adsorption may have been created by the edge interaction, and the sites apparently resembled those of 1/2-Mg–Co/SiO_2 in nature. Hence, the CO adsorption capacity was increased by the presence of MgO even though the extent of reduction decreased with increasing MgO content. Also, static chemisorption measurements indicated that the hydrogen uptake (table 2) increased for catalysts with a Mg : Co molar ratio of 2. Apparently the presence of MgO creates new types of active sites, most likely at the perimeter of the cobalt particles. These results contradict previous reports that the CO adsorption capacity decreases with MgO promotion [1,4,5].

In addition to CO, the catalyst surfaces desorbed CO_2 during TPD. The desorption of CO_2 was markedly altered by the presence of MgO, as shown in fig. 2. First of all, the Co/SiO_2 desorbed CO_2 in three stages, whereas the promoted catalysts did so in only two. The total amount of CO_2 desorbed decreased in the order 1/2-Mg–Co/SiO_2 > Co/SiO_2 > 2-Co–Mg/SiO_2 and 2-Mg–Co/SiO_2. As can be seen, the order of impregnation had no significant influence on the CO_2 desorption even though the molar ratio of Mg : Co on the surface of 2-Co–Mg/SiO_2 and 2-Mg–Co/SiO_2 was 1.4 and 3.8, respectively (table 2). Some of the CO_2 desorption may be attributed to the decomposition and desorption of the $Co(CO)_4^-$ and CO_3^{2-} species [12]. During the subsequent TPSR, Co/SiO_2 released water, whereas the MgO promoted catalysts released water, CO, and CO_2. Apparently, some of the surface species generated by the interaction of cobalt and MgO were stable under inert gas, but decomposed under hydrogen atmosphere.

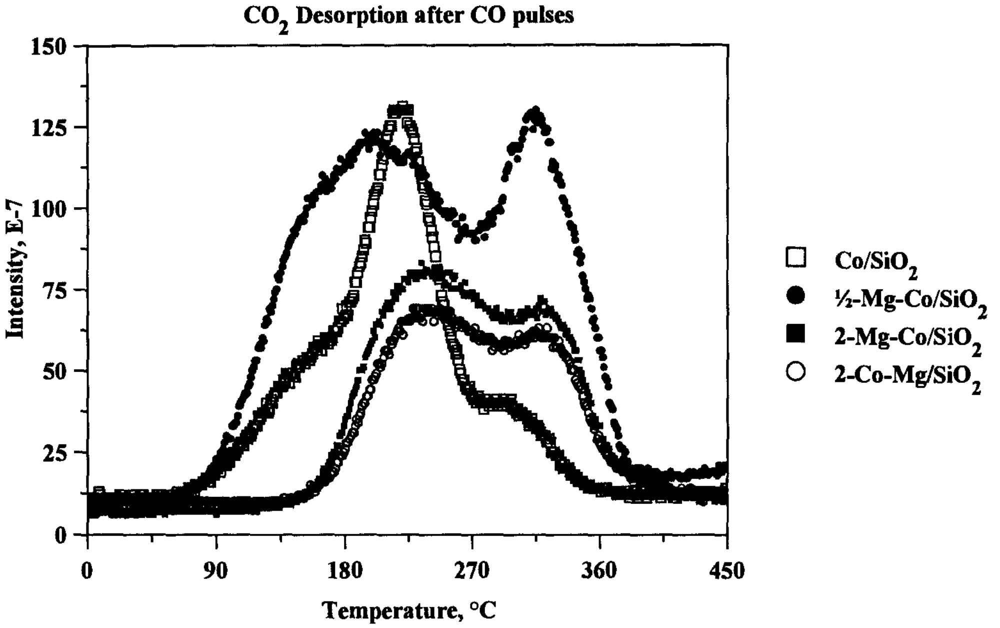

Fig. 2. CO_2 desorption from Co/SiO_2, $1/2$-Mg–Co/SiO_2, 2-Mg–Co/SiO_2 and 2-Co–Mg/SiO_2 after CO pulses at 25°C.

3.2.3. Initial reactivity

The CO pulses in the presence of hydrogen at 25°C resulted in the formation of methane and ethane. At 250°C the surface reactions also produced water and CO_2. The water evolution decreased with increasing amount of magnesium promotion, i.e. in the order $Co/SiO_2 > 1/2$-Mg–$Co/SiO_2 >$ 2-Mg–Co/SiO_2, 2-Co–Mg/SiO_2. However, the decreasing amount of water was not accompanied by increased formation of CO_2, which may be produced by the water–gas shift reaction (WGS) [21]. Lower CO_2 production (lower WGS activities) with alkaline earth promotion has been observed by Takeuchi et al. [22]. Plausibly, the effect of magnesium oxide was based on the modification of the active sites [4,9,13]. MgO is known to facilitate the formation of formate species by the reaction of CO and H_2O [9,11]. In fact, slight methanol formation has been observed with magnesium promoted catalysts.

3.3. STEADY-STATE STUDIES

The steady-state results showed the order of impregnation to influence the catalyst activity. When magnesium was impregnated after cobalt, the catalyst activity decreased, but when magnesium was impregnated first the activities were the same or higher relative to the unpromoted catalyst. The activities were related to the ratio of Mg : Co on the catalyst surface: the more active catalysts had more accessible cobalt. Closer attention was accordingly directed to $1/2$-Mg–Co/SiO_2

Table 3
Steady-state activities of catalysts reduced at 400°C and reacted at 0.5 MPa, GHSV 2600 h^{-1}

Catalyst on SiO$_2$	T (°C)	X_{CO} (%)	α	CO$_2$ (mol%)
Co	235	21	0.76	0.2
Co	260	45	0.66	10.3
Co	290	51	0.59	15.3
1/2-Mg–Co	235	20	0.77	2.5
1/2-Mg–Co	260	30	0.65	4.3
1/2-Mg–Co	290	25	0.52	4.1
2-Mg–Co	235	22	0.71	0.3
2-Co–Mg	235	27	0.66	3.3
2-Co–Mg	260	52	0.60	4.0
2-Co–Mg	290	47	0.50	7.2

and 2-Co–Mg/SiO$_2$. The differences in activity were observable particularly at the higher reaction temperatures of 260 and 290°C (see table 3). It should be noted that the probabilities of chain growth were slightly lower for the catalysts with Mg : Co molar ratio of 2, i.e. catalysts with lower extents of reduction, smaller particle size (XRD), and higher dispersion. Reuel and Bartholomew [23] have also observed that the molecular weight of hydrocarbon products is lower for cobalt catalysts having higher dispersions and lower extents of reduction.

The activity results at 235°C indicated that the catalysts promoted with magnesium were better able than their unpromoted counterparts to withstand higher reduction temperatures, i.e. their overall activity was maintained. The activity results of the catalysts reduced at 450°C were recalculated to obtain the activity per active cobalt site. The conversions were related to the extents of reduction and the dispersions of the catalysts as shown in table 4. The results indicate that the activity per available metallic site was clearly enhanced in the presence of magnesium as a result of increased dispersion and lower extent of reduction of the magnesium promoted catalysts. The highest activity was observed with 1/2-Mg–Co/SiO$_2$, though the activity of both 2-Mg–Co/SiO$_2$ and 2-Co–Mg/SiO$_2$ increased as well. A dis-

Table 4
Experimental results obtained at 0.5 MPa and 235°C with GHSV = 2600 h^{-1} and catalyst amount of 1 g

Catalyst on SiO$_2$	X_{CO} [a] (%)	X_{CO} [b] (%)	Dispersion (%)	Co (mg)	Reduction (%)	X_{CO} [c] (%/mg$_{met}$)	CO$_2$ [b] (mol%)
Co	21	11	5.5	51	54	7	2.2
1/2-Mg–Co	20	20	5.1	47	55	15	0
2-Mg–Co	22	22	12	44	35	12	0
2-Co–Mg	27	23	9.7	45	41	13	0

[a] Reduction at 400°C.
[b] Reduction at 450°C.
[c] X(%): [Co(mg) * D(%)/100 * R(%)/100].

tinct influence of the magnesium promotion was the observed disappearance of CO_2 from the product stream, an observation in agreement with our previous study [6] and supported by the pulse reaction studies.

4. Conclusions

We studied the effect of MgO promotion on silica supported cobalt catalysts prepared from nitrate precursors. The presence of MgO decreased the extent of reduction and increased the dispersion. The Co–MgO edge sites probably facilitated the adsorption of CO through species such as $Co(CO)_4^-$ and CO_3^{2-}. The Co–MgO sites apparently increased CO adsorption, and shifted the desorption of CO and CO_2 to higher temperatures. The desorption of CO and CO_2 was affected more by the ratio of Mg : Co in the bulk catalyst than by the Mg : Co atomic ratio on the upper surface. Also, some of the adsorbed species were stable during the TPD in He, but decomposed to CO and CO_2 in hydrogen atmosphere during TPSR.

The catalyst activity and product formation were related both to the impregnation order and to the molar ratio of Mg : Co in the bulk. Thus, MgO was effective in catalyst activity enhancement; the highest activity per metallic site available was obtained with a Mg : Co molar ratio of 1/2. The CO_2 formation was suppressed by increasing amounts of magnesium due to the chemical modification of the active sites. The presence of MgO on the surface likely facilitated the formation of formate species, which were subsequently hydrogenated to methanol.

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