

COMPARATIVE STUDIES OF LANTHANUM AND CERIUM AS PROMOTERS OF COBALT BASED FISCHER-TROPSCH CATALYSTS.

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INTRODUCTION

These last years, cobalt based catalysts have been widely developed in Fischer-Tropsch synthesis, particularly for the preparation of higher molecular weight fractions (chain growth probability $\alpha > 0.9$). The most studied catalysts are Co/Al₂O₃ or Co/SiO₂ undoped or doped by a second metal (Ru, Rh, Pt, Re...) and/or oxides (ZrO₂, TiO₂, rare earth oxides...) (1-5). The second metal generally favours the reduction of cobalt by hydrogen spillover phenomena or acts in regeneration of deactivated systems. The oxide operates through its interaction with the metal (TiO₂, ZrO₂), its reducibility (CeO₂), its acidic character (Al₂O₃) or the coverage of the metal particle by different processes including migration to the surface (La₂O₃). In the present work, a comparative study of Co/SiO₂ catalysts and lanthanum oxide or cerium oxide promoted Co/SiO₂ catalysts is reported. Results concerning the preparation, reduction and reactivity with syngas in a slurry type reactor are included.

EXPERIMENTALS

Preparation

A sol-gel type method has been developed (6) instead of a conventional successive impregnation technique, in order to be able to control the cobalt dispersion, even at high cobalt loadings (25 wt%). The overall scheme of preparation is as follows (Scheme 1).

Cobalt, cerium or lanthanum nitrate as well as tetraethoxysilane (TEOS) are dissolved separately in ethanol at 70°C. Once the solutions are mixed, precipitation is performed by adding an excess of oxalic acid dissolved in ethanol at 70°C. The released nitric acid makes the medium acidic, and during ethanol evaporation TEOS is slowly hydrolyzed by the water contained in the precursor salts. The evaporation is performed over a long period (6 hrs) until complete hydrolysis of TEOS. The catalysts are then dried (12 hrs, 100°C) and calcined (550°C, 4 hrs). The different catalysts prepared have the same cobalt weight content, and are described in Table 1.

Characterization Techniques

Temperature programmed reduction (TPR) :

TPR experiments were performed by passing pure hydrogen (12 ml.min⁻¹) over 0.2 g of calcined sample and a temperature increase rate of 1 K.min⁻¹ has been selected. The reduction was monitored by water formation as measured in the exit gas by a catharometer detector.

X-ray diffraction (XRD) :

The monochromatic X-ray beam was produced by a Cu anticathode

($\lambda = 1.5418 \text{ \AA}$) in a Siemens D5000 powder diffractometer. The XRD patterns were recorded for 2 values between 10 and 90° with a 0.005° spacing. Identification of the phases were made according to the JCPDS files.

X-ray Photoelectron Spectroscopy (XPS) :

The spectrometer was a Vacuum Generator's ESCA3 fitted with a preparation and an analysis chamber (10⁻¹⁰ Torr vacuum) (293 < T < 873 K). The deconvolutions were made both for the Co2p_{3/2} and Co2p_{1/2} peaks. The binding energies were measured by taking the C1s peak of contamination carbon at 284.8 eV as reference.

Transmission Electron Microscopy (TEM) :

The apparatus was a TESCON EM-002B type device (1.8Å resolution, 200kV acceleration potential). The analysis for chemical elements was performed by EDS with a KEVEC analyzer (selected area 14 nm). The powdered sample was suspended in ethanol and one drop of the suspension was deposited on a copper grid covered by a carbon membrane.

Reactivity test.

The catalytic tests were performed in a slurry bed reactor (7). Typical conditions were : $P = 2\text{MPa}$, $T = 493\text{K}$, $\text{H}_2/\text{CO} = 2/1$, $\text{G.S.H.V.} = 2000\text{ h}^{-1}$. The catalysts were reduced ex-situ at temperatures up to 513K under a flow of diluted hydrogen (5% H_2 in N_2) and then under a pure hydrogen flow with an increasing temperature up to 673K with a $1\text{K}\cdot\text{min}^{-1}$ slope and a final step at constant temperature (400K) for 14 hrs. The syngas mixture was admitted into the reactor at room temperature. The starting time for the reaction at 493K is taken after stabilization of the catalytic system.

RESULTS AND DISCUSSION

Characterization of the catalysts

Calcined catalysts

By thermogravimetric analysis (TGA), it is shown that cobalt, mixed cobalt-cerium or cobalt-lanthanum oxalates are decomposed between 543 and 603K. At 823K, part of the lanthanum is present as an oxycarbonate. In the XRD diffractograms and XPS spectra, cobalt is seen to be present as the Co_3O_4 spinel phase, ceria in a fluorite structure and lanthanum as an oxycarbonate but also as a LaCoCO_3 perovskite whose proportion increases with the amount of lanthanum added to the preparation.

The XPS analysis of the surface indicates that Co/Si ratio diminishes on the surface after calcination : 0.12 instead of the theoretical bulk 0.403 ratio for the Co/SiO_2 catalysts; 1.1 compared to 1.6 for $\text{Co-CeO}_2(\text{A})/\text{SiO}_2$; and 0.3 compared to 1.5 for $\text{Co-La}(\text{a})/\text{SiO}_2$.

This clearly shows that after calcination silica is segregated to the surface for the three series of catalysts. It must also be noted that cobalt silicate has not been evidenced. The NMR of silicium (MAS and CP-MAS) has shown that the initial silicagels are transformed to siloxane groups but some isolated silanol groups are also present.

The mean size of the cerium oxide crystallites has been evaluated to be about 80-85Å even for the catalysts with the highest cerium contents which indicates a very good dispersion of the promoter. Cerium oxide is present as aggregates and at the edge of these aggregates the CeO_2 and Co_3O_4 crystallites are in close contact with each other.

The size distribution of the cobalt oxide particles has been determined by TEM. The size distribution for $\text{Co-Ce}(\text{B})/\text{SiO}_2$ is represented on Figure 1. For Co/SiO_2 the mean size of cobalt oxide crystallites is about 300Å. It is much less (about 135Å) for $\text{Co-Ce}/\text{SiO}_2$ and for $\text{Co-La}/\text{SiO}_2$ (about 100Å). These results are in good agreement with those obtained by XRD (Figure 1).

The BET surface areas (Table 1) of the catalysts are large. They decrease upon addition of ceria or lanthanum oxide but remain higher than $100\text{ m}^2\cdot\text{g}^{-1}$. It must be noted that the Co/SiO_2 catalyst is microporous and that the mesoporosity increases with the amount of rare earth oxide (porous volume for $0.22\text{ cm}^3\cdot\text{g}^{-1}$ to $0.40\text{ cm}^3\cdot\text{g}^{-1}$).

Reduced catalysts

The reduction of all these catalytic systems has been followed by TPR and XPS. The TPR curves up to 753K (highest reduction temperature in the reactivity studies) for $\text{Co-Ce}/\text{SiO}_2$ and $\text{Co-La}/\text{SiO}_2$ are reported on figures 2 and 3.

The TPR curve for Co/SiO_2 shows two reduction peaks (543K, and a broad peak between 603 and 703K) (8). These two peaks are two widely separated to correspond to a two steps reduction of Co_3O_4 to Co^0 via CoO . It is suggested either that the reduction temperature changes is due to the change in the metal oxide particle size or that the microporosity of the catalyst makes the diffusion of the water produced during the reduction difficult, thus inhibiting the reduction process in the micropores.

For Co-Ce/SiO₂ (Figure 2) two reduction peaks are clearly present especially for the catalysts with the highest cerium contents. The first peak (483-513K) is shifted to lower temperature by increasing the cerium content. It corresponds to the reduction of Co₃O₄ to Co⁰. It is noteworthy that the presence of ceria lowers the reduction temperature of cobalt. The second peak corresponds to the reduction of ceria (the peak changes with the amount of CeO₂).

The Co-La/SiO₂ catalysts curves have also two maxima except for the highest loaded catalyst for which three maxima are observed (Figure 3). The three maxima are interpreted as the reduction of Co₃O₄ to Co⁰ (~ 553K), the reduction of the perovskite structure activated by the free cobalt (~ 613K) and the decomposition of carbonate species (> 723K). The extent of reduction of all the catalysts obtained by TPR, XPS and oxygen titration are summarized on Table 2.

As can be seen on Table 2, the cerium or lanthanum promoted catalysts are less reduced than the corresponding Co/SiO₂ catalyst (except for Co-La(a)/SiO₂). This point together with the lower initial cobalt oxide particle size (Table 1) will be important in the discussion of the catalytic reactivity results.

The cobalt particle size after reduction has been measured indirectly by reoxidation to Co₃O₄ followed by XRD analysis (Table 2). Compared to the calcined catalysts (Table 1), a decrease of the cobalt oxide particle size (240Å instead of 300Å), as well as a homogeneity for that of Co-Ce/SiO₂ (170, 165, 160 and 135Å for catalysts A, B, C, D respectively) and a slight decrease for Co-La/SiO₂ (120, 105, <100, <100Å) for catalysts a,b,c,d respectively) can be noted.

Catalytic reactivity tests.

All the characterized catalyst have been tested under the conditions described in the experimental part. The results are expressed as: total conversion of CO (CO%), conversion to hydrocarbons (HC%) and CO₂ (CO₂%), and productivity in hydrocarbons (kg.kgat⁻¹h⁻¹). The specific activity TOF¹ (mole h⁻¹) is defined as the number of CO moles transformed by gram of catalyst and unit time and TOF² (mole h⁻¹) as the number of CO moles transformed by cobalt metal site and unit time. The selectivity is expressed in mass per cent on a carbon basis. Table 3 gives the reactivity results for all the catalysts.

It can be noted that the CO conversion and TOF¹ are nearly the same for all the catalysts. For the promoted catalysts, TOF² decreases with the promoter content. TOF² values are higher for ceria than for lanthana. For some catalyst samples (B and D), they are higher than for Co/SiO₂. Selectivities are reported in Table 4.

The chain growth probability α deduced from the distribution of the hydrocarbons is 0.92 for Co/SiO₂. This value decreased for catalysts doped by ceria [from 0.87 (A) to 0.82 (D,C)] or lanthana [(0.88 (b), 0.82 (a)]. It can be noted the low amounts of promoters (5wt %) are sufficient to induce this decrease. A closer examination of the selectivities obtained shows that as soon as ceria or lanthana are added (Figure 4) :

- The methane selectivity changes drastically. (The mass fraction of CH₄ is increased by a factor of 2 or 3). The formation of methane depends on the amount of ceria or lanthana added.
- The C₅+ mole % fraction decreases strongly upon addition of Ce or La (80.0% for Co/SiO₂ compared to less than 60.0% for Ce and La containing catalysts).
- The mass fraction of C₂₂+ hydrocarbons is divided by 3.
- The C₅-C₁₃ fraction is favoured in the presence of cerium or lanthanum. The tendency has already been reported for Co-Ce/C tested under atmospheric pressure (9).

From these results it can be seen that the cerium or lanthanum promoted catalysts have about the same activity as the unpromoted ones, however the changes in hydrocarbon distribution are more significant : lower α values, higher methane formation, increase of the C₅-C₁₃ fraction and diminution of C₂₂+ yields. The change in hydrocarbon distribution can be attributed to several factors :

- The presence of smaller cobalt crystallites (240, 135-170 and 100-135Å for Co/SiO₂, Co-Ce/SiO₂ and Co-La/SiO₂) respectively.
- A higher extent of reduction for the promoted catalysts.

- The intrinsic properties of ceria or lanthana which can form hydrocarbons by themselves (10). On the catalysis containing cerium or lanthanum, hydrogen chemisorption and desorption experiments (Table 5) show clearly the influence of the promoter on hydrogen desorption. Both promoters act as hydrogen storage agents and thus probably influence the hydrocarbon selectivity of these catalysts (methane formation, decrease of chain growth).
- Modification of the nature of the cobalt site by interaction between cobalt and the rare earth, changing the CO and H₂ chemisorption properties.

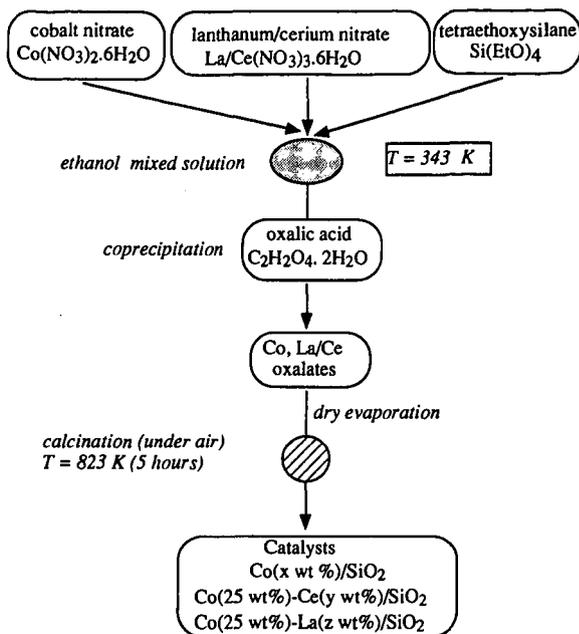
CONCLUSION

The present work has evidenced the modifications of the catalytic behaviour of 25 wt%Co/SiO₂ catalysts, when they are promoted by varying amounts of ceria or lanthana. The main changes were found in the cobalt particle size, the reducibility of the metal, and the ability to desorb previously adsorbed hydrogen from the catalyst.

The changes of physical properties of the catalysts have few consequences on the catalytic activity, but strongly influence the hydrocarbons distribution. Addition of CeO₂ or La₂O₃ enhances methane formation, increases the selectivity in the C₅-C₁₃ fraction and decreases the chain growth probability α .

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Scheme 1: Catalyst preparation procedure.

Catalysts	Co	Si	Ce or La	O	BET surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Particle size* cobalt oxide (\AA)
Co/SiO ₂	25.2	28.4	/	46.1	293	300(300)
Co-Ce(A)/SiO ₂	25.5	7.4	38.2	26.0	137	185
Co-Ce(B)/SiO ₂	25.5	16.9	21.5	34.6	103	170(135)
Co-Ce(C)/SiO ₂	24.6	23.5	8.9	42.7	281	165
Co-Ce(D)/SiO ₂	23.9	25.0	4.8	43.2	245	185
Co-La(a)/SiO ₂	24.9	6.9	37.5	28.1	123	125(110)
Co-La(b)/SiO ₂	24.5	16.0	21.2	34.8	131	125
Co-La(c)/SiO ₂	24.3	20.8	9.1	43.0	340	100
Co-La(d)/SiO ₂	24.8	26.4	4.7	43.4	384	110

* oxygen titration (TEM measurement)

Catalysts	Reduction extent (%)			Co particle size after reoxidation (\AA)
	TPR	XPS	Oxygen titration	
Co/SiO ₂	73	82	77	240
Co-Ce(A)/SiO ₂	66	89	89	170
Co-Ce(B)/SiO ₂	52	-	81	165
Co-Ce(C)/SiO ₂	51	-	77	160
Co-Ce(D)/SiO ₂	40	-	52	135
Co-La(a)/SiO ₂	80	84	81	120
Co-La(b)/SiO ₂	65	-	76	105
Co-La(c)/SiO ₂	64	-	65	<100
Co-La(d)/SiO ₂	39	-	42	<100

	Conversion			HC	TOF ¹	TOF ²
	CO%	HC%	CO ₂ %	productivity	(b)	(c)
				(a)		
Co/SiO ₂	10.8	10.7	0.0	68.9	12.7	43.6
Co-Ce(A)/SiO ₂	11.8	11.4	0.1	50.6	13.7	36.7
Co-Ce(B)/SiO ₂	13.6	13.1	0.1	53.5	15.8	52.0
Co-Ce(C)/SiO ₂	9.5	8.6	0.5	37.9	11.4	34.3
Co-Ce(D)/SiO ₂	12.9	12.6	0.1	54.6	15.9	55.3
Co-La(a)/SiO ₂	11.6	11.2	0.2	37.2	13.9	21.7
Co-La(b)/SiO ₂	10.0	9.6	0.1	41.5	11.8	22.6
Co-La(c)/SiO ₂	14.2	12.9	0.1	56.8	16.3	26.3
Co-La(d)/SiO ₂	12.3	12.0	0.2	53.9	14.5	38.8

(a) 10⁻³ kg . kgcat⁻¹.h⁻¹ (b) 10⁻³ mole h⁻¹ (c) 10⁻² mole h⁻¹

Catalysts	Mass selectivity (%)					
	C ₁	C ₂ -C ₄	C ₅ -C ₉	C ₁₀ -C ₁₃	C ₁₄ -C ₂₁	C ₂₂ ⁺
Co/SiO ₂	15.9	2.5	3.1	11.5	24.6	42.4
Co-Ce(A)/SiO ₂	34.0	9.2	12.3	15.4	15.9	13.2
Co-Ce(B)/SiO ₂	30.1	9.7	16.6	16.6	15.7	11.3
Co-Ce(C)/SiO ₂	46.6	8.3	10.0	13.9	14.8	6.4
Co-Ce(D)/SiO ₂	49.1	5.6	5.8	10.4	17.5	11.6
Co-La(a)/SiO ₂	48.4	6.5	7.0	16.5	14.7	6.8
Co-La(b)/SiO ₂	47.7	7.1	3.3	8.9	12.9	20.1
Co-La(c)/SiO ₂	38.9	5.9	15.2	15.2	14.2	10.6
Co-La(d)/SiO ₂	43.4	6.6	6.1	14.0	16.7	13.2

Catalysts	Chemisorbed H ₂ (μmole.g cat ⁻¹)	Desorbed H ₂ (μmole.g cat ⁻¹)
Co/SiO ₂	11.4	4.5
Co-Ce(A)/SiO ₂	14.5	30.4
Co-La(a)/SiO ₂	14.8	28.3

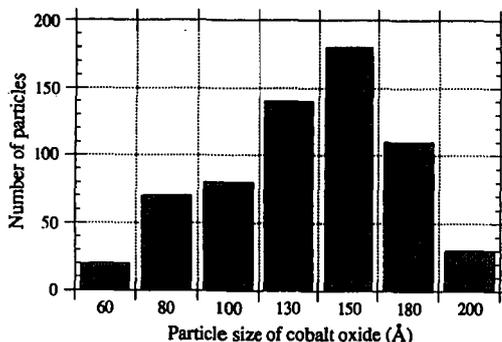


Figure 1. Cobalt oxide particle size distribution for Co-Ce(B)/SiO₂ catalyst.

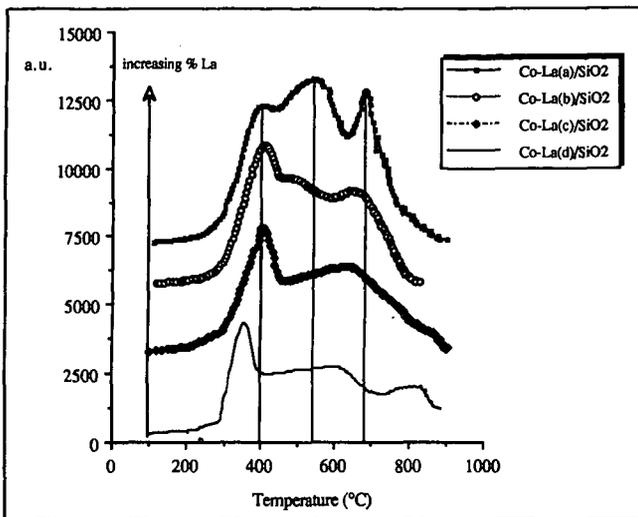


Figure 2. TPR curves for Co-La/SiO₂ catalyst.

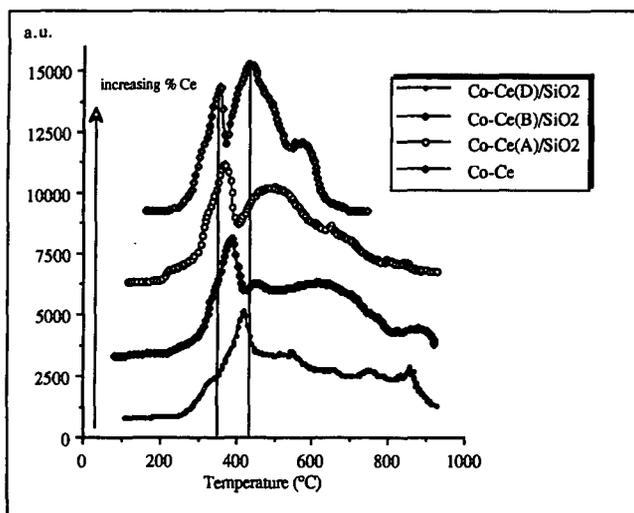


Figure 3. TPR curves for Co-Ce and Co-Ce/SiO₂ catalysts.

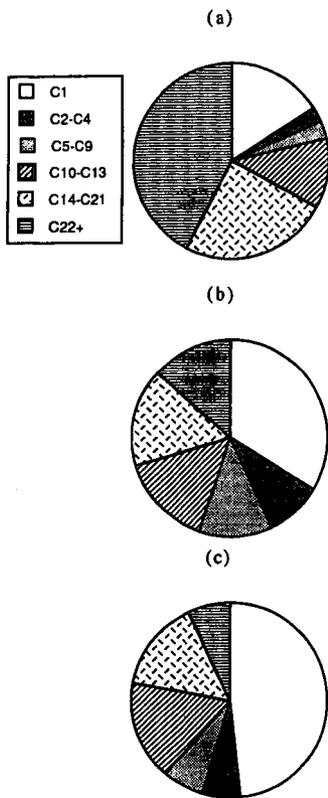


Figure 4. Weight distribution of hydrocarbons on (a) Co/SiO₂ (b) Co-Ce(A)/SiO₂ and (c) Co-La(a)SiO₂ catalysts.