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Fischer Tropsch reaction from a mixture similar to biosyngas. Influence of promoters on surface and catalytic properties of Co/SiO_2 catalysts

N. Escalona, C. Medina, R. García, P. Reyes *

Departamento de Físico-Química, Facultad de Ciencias Químicas, Universidad de Concepción, Concepción, Chile

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ABSTRACT

Fischer Tropsch reaction using a mixture similar to that obtained from biomass transformation (biosyngas) has been studied on promoted Co/SiO_2 catalysts. As promoters, Cu, Zn, Re and Ru at two different contents were analysed. The promoter affects both the reducibility and the dispersion of Co species, which have an important effect in the activity and selectivity of the studied catalysts. Re and Ru significantly increase both the activity and the selectivity to long chain hydrocarbons, whereas in those promoted by Cu and Zn the effect is strongly affected by the amount of promoter. In those with higher amount of promoter (0.5 wt%), the formation of surface spinels or the blocking of the Co active sites by the copper itself produces a drop in the catalytic activity. The product distribution of the liquid extract reveals the presence of hydrocarbons from C_6 to higher than C_{14+}, in most of the catalysts.

1. Introduction

Global warming has pushed the necessity to reduce the emissions of gases responsible for the Greenhouse effect, mainly CO_2. Public transportation produces approximately 22% of the total CO_2, because of the use of fossil fuels [1]. Nowadays, the Fischer Tropsch synthesis (FTS) is being used to synthesise hydrocarbons with different chain lengths from methane, having a H_2/CO molar ratio of 2. Different catalysts have been used in the FTS, the main active phases [2,3] being Co, Fe and Ru. Biomass appears as an attractive alternative as a clean, renewable and sustainable energy source. Different transformation routes have been used to convert biomass in liquid or gaseous fuels [4–6]. Thus, by biomass gasification a gas mixture called biosyngas is obtained containing H_2, CO, CO_2, and CH_4 with a H_2/CO molar ratio close to 1 [7,8]. Several papers have shown that it is technical and economically feasible to obtain liquid hydrocarbons from biomass using integrated systems of gasification and catalytic FTS reaction [5,9,10].

Most of the studies performed in the FTS have used the syngas as reaction mixtures and only a rather limited paper has been focussed to study the influence of reaction conditions and the type of catalysts on the activity and selectivity in the FTS using a biosyngas mixture [11–13].

The aim of the present work is to study the effect of the addition of Zn, Cu, Ru and Re at two different loadings (0.1 and 0.5 wt%) as promoters of a 20 wt% Co/SiO_2 catalyst in the FTS using a reactant mixture similar to that of biosyngas.

2. Experimental

2.1. Catalyst preparations

Promoted-Co supported catalysts were prepared using a SiO_2 (D11-11 $S_{BET} = 136\ m^2\ g^{-1}$) as support. The support was impregnated with an aqueous solution of cobalt nitrate to get 20 wt% of Co (expressed as metallic cobalt) catalyst, whereas those bimetallics were prepared by the co-impregnation of the support with the aqueous solution of cobalt nitrate and the precursor of the second metal in appropriate amount to obtain 20 wt.% of Co and 0.1 and 0.5 wt.% of M (being M = Cu, Zn, Re or Ru). As precursor of the second metal, $Cu(NO_3)_2$, $Zn(NO_3)_2$, NH_4ReO_4 and $RuCl_3 \times \cdot H_2O$ were used. The Co loading was chosen according to the previous results [13]. The solids were dried overnight at 120 °C and then calcined at 300 (Co–Re and Co–Ru) or 500 °C (Co–Cu and Co–Zn). The reduction was carried out in flowing hydrogen at 500 °C, prior characterisation or catalytic evaluation.

2.2. Catalyst characterisation

The specific surface area was evaluated from the adsorption of N_2 at 77 K in an automatic Micromeritics system Model ASAP 2010. Temperature programmed reduction (TPR) studies were carried out in a conventional system having a thermal conductivity detector and a quartz cell. In each experiment 100 mg of the sample was used, with a heating rate of 10 °C min^{-1} and the

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* Corresponding author. Fax: +56 41 2245974.
E-mail address: preyes@udec.cl (P. Reyes).

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temperature range from 25 to 1050 °C. The mixture used in the reduction experiments was a 5% H_2/Ar with a flow of 50 cm^3/min. The metal particle size distributions were obtained from transmission electron microscopy (TEM) micrographs, taken with a Jeol Model JEM-1200 EXII System. X-ray photoelectron spectra (XPS) were acquired with a Fisons ESCALAB MkII 200R spectrometer equipped with a hemispherical electron analyser and an Al K_α ($h\nu$ = 1486.6 eV, 1 eV = 1.602×10^{-19} J) 120 W X-ray source. Prior to the analysis, the samples were reduced *in situ* in H_2 flow at 773 K for 4 h. All binding energies (BE) were referenced to the Si 2p line at 103.4 eV. This reference gave BE values within an accuracy of ±0.2 eV. Atomic ratios were calculated from the intensity ratios normalised by atomic sensitivity factors.

2.3. Catalytic reaction

Catalytic activity measurements were carried out in a fixed bed stainless steel reactor. The reaction conditions were space velocity (GHSV) of 1800 ml g^{-1} h^{-1}, pressure of 10 atm and reaction temperature of 300 °C. The reactant was a representative mixture obtained from the biomass gasification having $H_2/CO/CO_2/CH_4/N_2$ in the molar proportions 32%/32%/12%/18%/6%, respectively [7]. Prior to the reaction, the catalysts were reduced *in situ* at 500 °C during 10 h under hydrogen flow. Catalytic measurements were obtained at a steady state, approximately after 80 h on stream. The analyses of products were performed by gas chromatography using a Perkin Elmer 3920B system provided with a thermal conductivity detector, using a n-octane porasil-C column for liquids and a carbosieve II column for the gaseous products.

3. Results and discussion

Table 1 compiles the specific surface area and metal particle size of Co promoted catalysts. It can be seen that the surface area is almost not affected by the addition of a promoter as expected. The metal dispersion is very low and TEM results revealed that the promoter produces a decrease in the average metal particle size. However, this result is a consequence of a broadening in the metal particle size distribution; thus, the monometallic Co catalyst displays a rather narrow distribution with most of the particles being in the range 40 ± 5 nm. Meanwhile in those promoted, a significant fraction of smaller particles close to 5 nm and also of larger sizes higher than 100 nm appears. This result is in line with the increases in the particle size detected by XRD (not shown here).

Table 1
Specific area (S_{BET}) and cobalt particle size estimated from TEM of Co–M (0.5)/SiO_2 catalysts.

Catalyst	S_{BET} (m^2 g^{-1})	TEM (nm)
Co/SiO_2	113	41
CoCu/SiO_2	106	34
CoRe/SiO_2	108	37
CoRu/SiO_2	104	34
CoZn/SiO_2	105	30

TPR profiles of the studied samples are given in Fig. 1a and b. The profile of the samples promoted with Cu, Zn and Re with low promoter content displays a slight shift towards higher temperatures in the Ru and the shifts are to a lower temperature. This fact may be understood considering that the simultaneous presence of Cu (or Zn) and Co may lead during calcinations to a mixed oxide (spinel type structures), which is more difficult to reduce than the simple oxides. The reduction of Re oxides also takes place at higher temperatures than the cobalt oxides. Conversely, ruthenium oxide is reduced at lower temperature and by hydrogen spillover catalyses the reduction of cobalt oxides at lower temperatures (Tables 2 and 3).

XP spectra of Co $2p_{3/2}$ core level of the reduced samples showed the presence of Co^0 and Co^{2+} species and the extent of reduction is higher in the promoted samples, especially in those with Re and Ru due to the higher ability to dissociate hydrogen. Additionally, a slight enhancement in the Co/Si ratio in those samples promoted by Cu, Zn and Re accounts for the higher dispersion of the bimetallic samples compared to the Co/SiO_2 catalyst. The increase

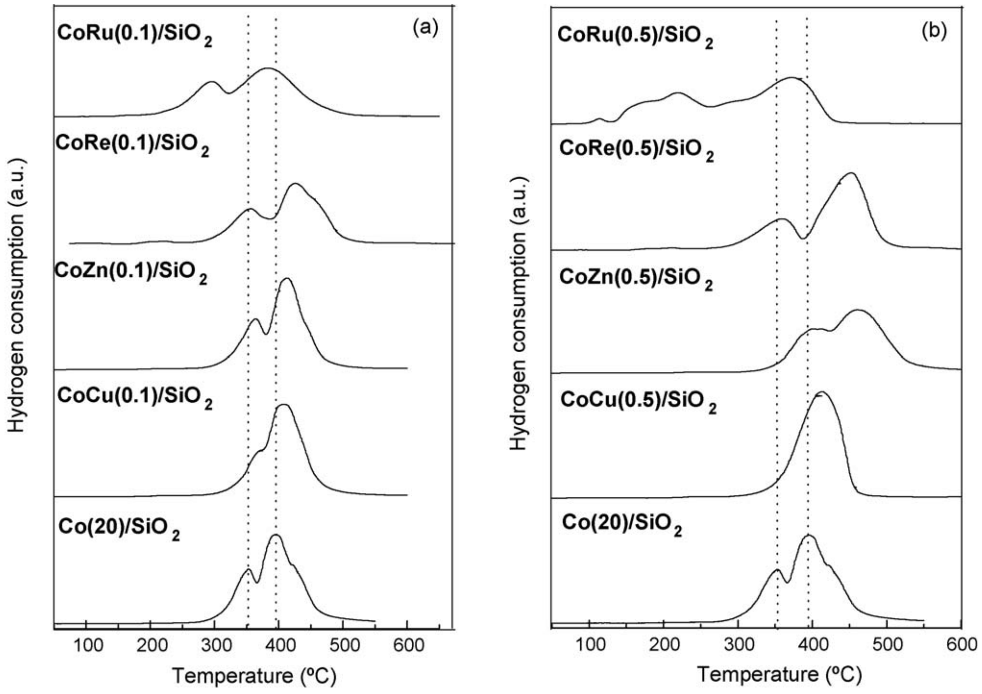

Fig. 1. Temperature programmed reduction profiles of Co–M/SiO_2 catalysts (a) series with 0.1 wt% of promoter and (b) series with 0.5 wt% of promoter.

Table 2
Binding energies of Si 2p, O 1s and Co 2p and Co/Si atomic surface ratios of reduced Co(20)M(0.1)/SiO_2 catalysts M = Cu, Re, Ru, Zn.

Catalyst	BE (eV) Si 2p	BE (eV) Co $2p_{3/2}$	$(Co/Si)_s$
Co/SiO_2	103.4	778.1 (62) 780.5 (38)	0.043
CoCu/SiO_2	103.4	778.0 (82) 780.4 (18)	0.045
CoRe/SiO_2	103.4	778.0 (87) 780.4 (13)	0.043
CoRu/SiO_2	103.4	778.0 (88) 780.4 (12)	0.137
CoZn/SiO_2	103.5	778.0 (65) 780.1 (35)	0.053

Bulk Co/Si atomic ratio = 0.255.

Table 3
Binding energies of Si 2p, O 1s and Co 2p and Co/Si atomic surface ratios of reduced Co(20)M(0.5)/SiO_2 catalysts M = Cu, Re, Ru, Zn).

Catalyst	BE (eV) Si 2p	BE (eV) Co $2p_{3/2}$	$(Co/Si)_s$
Co/SiO_2	103.4	778.1 (62) 780.5 (38)	0.043
CoCu/SiO_2	103.4	777.9 (80) 780.5 (20)	0.045
CoRe/SiO_2	103.4	777.9 (90) 780.3 (10)	0.050
CoRu/SiO_2	103.4	778.9 (90) 780.3 (10)	0.112
CoZn/SiO_2	103.5	778.1 (67) 780.3 (33)	0.055

Bulk Co/Si atomic ratio = 0.255.

Table 4
Activity and selectivity results under steady state conditions in the Fischer Tropsch reaction over Co–M/SiO_2 catalysts at 300 °C and 10 bar.

Catalyst	Promoter (%)	Conversion CO (%)	Selectivity (C mol%)		
			CH_4	CO_2	C_{5+}
Co/SiO_2	0	25.8	93.5	0.4	6.1
CoCu/SiO_2	0.1	12.3	84.3	12.8	2.9
CoRe/SiO_2	0.1	29.7	80.3	3.3	16.4
CoRu/SiO_2	0.1	32.3	84.8	6.6	8.6
CoZn/SiO_2	0.1	28.9	86.2	9.3	4.5
CoCu/SiO_2	0.5	8.3	77.5	22.3	0.2
CoRe/SiO_2	0.5	32.2	82.1	8.3	9.6
CoRu/SiO_2	0.5	29.6	85.9	6.5	7.6
CoZn/SiO_2	0.5	22.6	85.4	7.1	7.5

in that ratio is much higher in those promoted with Ru, indicative of a higher dispersion degree, in line with the TEM results.

The observed changes may be understood on the basis of the precursors and support interaction. The cobalt nitrate solution has a pH of 5.56, the pH values being 5.56, 5.49 and 5.10 for Co–Re, Co–Zn and Co–Cu solutions, respectively. Upon the addition of the silica support the pH value drops to 4.22 ± 0.30 for these samples. On the other hand, in the Co–Ru system the pH of the solution was 2.90 and decreases to 2.73 after silica addition. The isoelectric point of SiO_2 is 1–2 pH units. Therefore, differences in the interaction between metal precursor and support should exist. Thus, even Co–Re, Co–Zn and Co–Cu systems exhibit similar features; Re is present in anionic form whereas the others are cations, having different sites for anchorage on the support. The pH in these systems was almost the same, close to 4.2, and cobalt should be present as Co^{2+} and $CoOH^+$ species, whereas in the Co–Ru system once the support was added the pH decreases to 2.73, Co being present at this pH essentially as Co^{2+}. After calcination and reduction treatments, the former species display a higher trend to form larger agglomerates than Co–Ru system.

Catalytic studies of the prepared catalysts were performed at 300 °C and 10 atm of pressures using a gas mixture similar to biosyngas with a mole% composition of H_2:CO:CO_2:CH_4:N_2 of 32:32:12:18:6. The reaction was studied for at least 24 h, reaching a steady state after 8 h on stream. Table 4 compiles the conversion level and selectivity under steady state at 300 °C and 10 atm for the studied catalysts. It can be seen that for low promoter content (0.1 wt%), the conversion of CO increases from approximately 26% for the Co/SiO_2 to values close to 32% for the promoted samples, except that promoted by Cu which exhibits a very low conversion level, close to 12%. In the series with 0.5 wt% of promoter the drop in the activity in the CoCu catalysts is even more drastic, reaching a conversion level of 8.3% and the CoZn catalyst also displays a decrease in the conversion compared with the monometallic Co/SiO_2 catalyst. Even though the cobalt particle size is smaller in the promoted samples, especially in which the promoter content is higher, and the reduction degree is higher, therefore, an enhancement in the catalytic activity should be expected in those samples promoted with Zn and Cu, and the opposite behaviour was observed, which may be interpreted considering that in these samples the formation of spinel type oxides as a consequence of calcinations should be expected, thus reducing the extent of active sites. The presence of these mixed oxide species has already been reported for other systems. Other possibility for this behaviour is the blocking of the Co active sites by the copper itself. However, due to the small amount of promoter they were not detected in the present work either by XRD or by XPS.

Table 4 also shows the selectivity to CH_4, CO_2 and C_{5+} for the studied catalysts. High selectivity to CH_4 was observed for all catalysts, being even more higher for the unpromoted Co catalyst. The condensable products, expressed as hydrocarbons with C length higher than C_5, are mainly obtained in those catalysts promoted by Ru and Re, with selectivity levels close to 10% or even higher in the CoRe (0.1) sample. The presence of the promoter produces a shift in the product distribution as can be seen in Fig. 2a and b. Thus, Co/SiO_2 catalyst showed a distribution with a higher proportion of C_8–C_{11} whereas in the promoted Co catalysts the distribution is wider, increasing the proportion of larger hydrocarbons. This effect occurs in a higher extent as the promoter content increases. This fact is attributed to a decrease in the metal particle size in agreement with the previous results [13]. Moreover, the promoter, mainly Re and Ru, leads to a higher reduction degree of cobalt oxides and by hydrogen spillover contributes to maintain the cobalt species in a reduced state, inhibiting the deactivation of the catalyst and it is also known that the presence of cobalt oxides (detected by XPS) promotes the formation of short chain hydrocarbons. It should be mentioned that the Co–Cu catalyst with 0.5 wt% of Cu did not produce liquid hydrocarbons, which may be attributed to the formation of highly dispersed $CuCo_2O_4$ spinels to the blocking of the Co active sites by the copper itself.

On the other hand, Table 4 also gives the selectivity to CO_2 for the studied samples in which CoCu catalysts display the highest values (12.8–23.1%), for the other promoters being close to 6%.

To account the formation of CO_2, Krishnamoorthy et al. [14] proposed a model based on the adsorption and dissociation of CO on the surface of carbon, where the hydrogen does not play any role, as shown in the following reactions:

$$CO \rightarrow C_a + O_a$$

$$O_a + CO \rightarrow CO_2$$

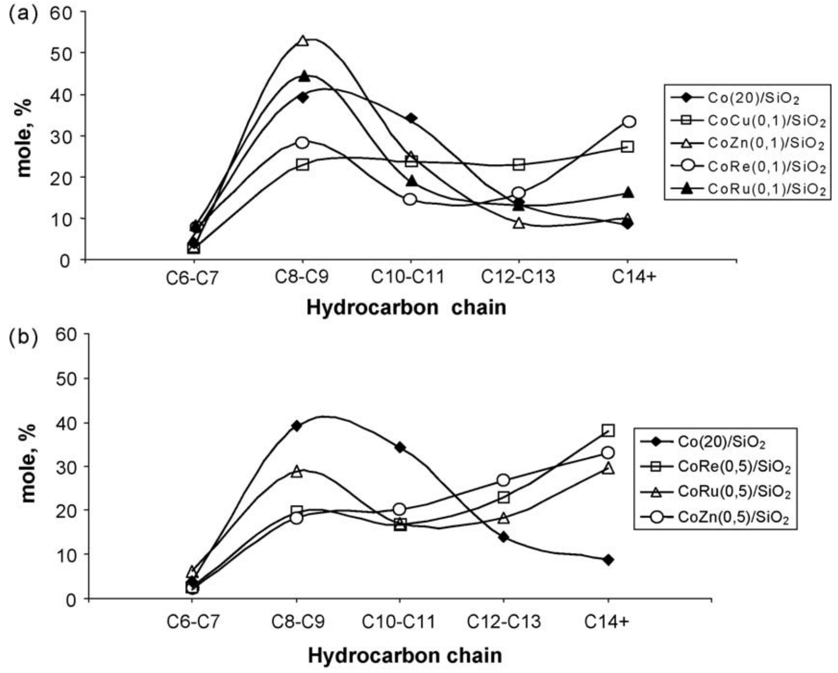

Fig. 2. Product distribution in the liquid extract produced in the Fischer Tropsch reaction over Co–M/SiO_2 catalysts at 300 °C and 10 bar. (a) Series with 0.1 wt% of promoter and (b) series with 0.5 wt% of promoter.

4. Conclusions

The obtained results showed that using a mixture similar to the biosyngas is possible to obtain liquid hydrocarbons on Co and promoted Co catalysts. The liquid hydrocarbons have a length chain from C_6 to larger than C_{14+}.

The distribution of liquid hydrocarbons depends on the Co particles size and the reduction degree of cobalt species. Smaller metal particles and highly reduced cobalt contribute to the formation of hydrocarbons with higher chain lengths. In the present study Co–Re and Co–Ru catalysts are those with higher activity and selectivity to higher hydrocarbons.

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References

[1] http://www.ipcc.ch/pdf/assessment-report/ar4/syr/ar4_syr.pdf.
[2] H. Schulz, Appl. Catal. A 186 (1999) 3.
[3] M.E. Dry, Catal. Today 71 (2002) 227.
[4] A. Demirbas, Prog. Energy Combust. Sci. 33 (2007) 1.
[5] M.J.A. Tijmensen, A.P.C. Faaij, C.N. Hamelinck, M.R.M. van Hardeveld, Biomass Bioenergy 23 (2002) 129.
[6] G.W. Huber, S. Iborra, A. Corma, Chem. Rev. 106 (2006) 4044.
[7] K. Tomishige, M. Asadullah, K. Kunimori, Catal. Today 89 (2004) 389.
[8] S.T. Chaudhari, S.K. Bej, N.N. Bakhshi, A.K. Dalai, Energy Fuels 15 (2001) 736.
[9] M.J. Prins, K.J. Ptasinski, F.J.J.G. Janssen, Fuel Process. Technol. 86 (2005) 375.
[10] C.N. Hamelinck, A.P.C. Faaij, H. den Uil, H. Boerrigter, Energy 29 (2004) 1743.
[11] K.-W. Jun, H.-S. Roh, K.-S. Kim, J.-S. Ryu, K.-W. Lee, Appl. Catal. A 259 (2004) 221.
[12] A. Lapidus, A. Krylova, Y. Paushkin, J. Rathouský, A. Zukal, J. Stárek, Fuel 73 (1994) 583.
[13] C. Medina, R. García, P. Reyes, N. Escalona, 21st Iberoamerican Sym. Catal. Benalmadena, Malaga, Spain, June 2008.
[14] S. Krishnamoorthy, A.W. Li, E. Iglesia, Catal. Lett. 80 (2002) 77.