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Re–Co/Al_2O_3 bimetallic catalysts prepared by mechanical treatment: CO hydrogenation and CH_4 conversion

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Abstract

Re–Co/Al_2O_3 (M) bimetallic catalysts were prepared by ball milling in a high-energy shaker mill using a WC container and four WC balls. The structure and activity of the Re–Co/Al_2O_3 (M) are compared to a Re–Co/Al_2O_3 (IM) sample prepared by the incipient wetness technique. The mechanically treated sample contains disordered, probably partly amorphous metal particles. Heat treatment of the Re–Co/Al_2O_3 (M) sample was carried out in hydrogen at 450 and 650 °C. It affects the crystallinity and the catalytic properties of the metal particles.

The rate measured for the CO hydrogenation over Re–Co/Al_2O_3 (IM) catalyst is significantly higher than that measured over the Re–Co/Al_2O_3 (M) sample. On the other hand, in the CH_4 conversion to higher hydrocarbons, the Re–Co/Al_2O_3 (M) showed higher activity after treatment at 650 °C. The opposite behavior of the M and IM samples is explained by the changing morphology of the active sites responsible for the two different reactions.

Keywords: Mechanical treatment on Co–Re/Al_2O_3; CO hydrogenation; Activity; Selectivity; CH_4 conversion

1. Introduction

Alumina-supported bimetallic cobalt catalysts seems to be a primary choice for producing high molecular weight hydrocarbons [1]. Rhenium, having been applied in the reforming technologies, proved to be an effective modifier of the structure and activity of iron and cobalt catalysts. The addition of 10 at.% Re to an Fe/Cab–O–Sil catalyst increased the rate of CO hydrogenation by a factor of 15, leaving the olefin selectivity at around 80%. The effect was explained by stabilization of the small iron particles by rhenium-oxide, hampering the migration of iron nanoparticles on the surface of Al_2O_3 [2,3]. Although the formation of Re–Co nanoparticles in Re–Co/Al_2O_3 was reported recently [4,5], the phenomenon causing the enhanced activity has not been clarified yet.

The mechanical agitation of solid samples creates dislocations, internal strains and stacking faults that obviously increase the surface reactivity in various reactions. The stability of defects is high in oxides as has been shown in various mixed oxide systems [6–11]. Considerably fewer data can be found in the literature on metals, where stabilizing the structural defects is more difficult [12–14]. For instance, previous studies on the Raney Ni–Fe system showed a promotional effect on the activity for benzene hydrogenation that was

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attributed to the presence of Ni and $NiFe_2O_4$ phases. High temperature treatment converted the entire Ni content into the low-activity $FeNi_3$ phase [13].

In the present study the preparation of rhenium–cobalt bimetallic catalysts is attempted from a mixture of the two metal powders and γ-Al_2O_3 by mechanical alloying and the defects formed in the metals are stabilized by appropriate heat treatment. The mechanically prepared catalysts mimic the alumina-supported bimetallic system. X-ray diffraction (XRD) and temperature programmed reduction (TPR) are used for characterization and the two-step methane conversion to higher hydrocarbons as well as the CO hydrogenation for testing the catalytic activity of the samples.

2. Experimental

2.1. Preparation of samples

The samples were prepared by ball milling using a high-energy shaker mill (SPEX 8000) with WC milling container and four WC balls, 1 cm in diameter. Milling was carried out in argon atmosphere. The starting materials were metallic cobalt and rhenium powders, 99.8% pure, finer than 50 μm, obtained from Alfa and nanoscale alumina powder (γ-Al_2O_3) obtained from Nanophase Technologies. In order to ensure efficient mixing between the metal components, a mixture of 1.8 g cobalt and 0.2 g rhenium powders was milled for 1 h. The resulting powder was mixed with 2.4 g of γ-Al_2O_3 and milled under the same conditions for an additional 3 h. The mechanically treated Re_3Co_{97}/Al_2O_3 sample (denoted as Re–Co/Al_2O_3 (M)) was compared with a $Re_{10}Co_{90}/Al_2O_3$ catalyst prepared by the incipient wetness technique (denoted as Re–Co/Al_2O_3 (IM)). The total metal loading was 45 and 10 wt.% for samples M and IM, as determined by X-ray fluorescence spectroscopy.

2.2. Characterization

The samples were characterized by TPR using 1 vol.% hydrogen/argon mixture with 10 °C min^{-1} ramp rate. A SORBSTAR apparatus, equipped with QMS type Hiden HAL 02/100 was employed and the measurement was carried out on "as-milled" samples, after hydrogen and after oxidation.

X-ray powder diffraction was recorded using an X'Pert XRD system with Cu tube, theta–theta geometry and a graphite monochromator with proportional chamber detector. The measurements were carried out in an Anton Paar HTK 1200 oven. The as-milled sample was annealed consecutively at 250, 350, 450 and 650 °C for 1 h in flowing H_2 and XRD was recorded both at temperature and after cooling the sample to room temperature between annealings. The H_2 gas flow was kept on during the entire process.

2.3. Catalytic reaction

The CO hydrogenation was carried out in the differential regime at 10 bar pressures and temperatures between 230 and 280 °C. The performance of Re–Co/Al_2O_3 (M) was compared to samples of Re–Co/Al_2O_3 (IM), Re–Co/SiO_2 (SG) prepared by sol/gel methods [10] and Re–Co/NaY (IM) prepared by incipient wetness technique. The samples were treated in hydrogen at 400 °C for 2 h prior to the catalytic reaction. Another possible C_1 reaction, two-step methane conversion, was also used as a test reaction. It was measured in a pulse system according to the following protocol: 100 mg catalyst was reduced in hydrogen at 400 °C for 1 h. Then, a 0.5 cm^3 (22.3 μmol) methane pulse was introduced at a flow rate of 100 $cm^3\,min^{-1}$ at 450 °C. It was followed by flushing with He and treated with a 50 vol.% H_2/He mixture at 150 °C with a total flow rate of 100 $cm^3\,min^{-1}$ unless otherwise indicated.

The reaction products were analyzed by means of a gas chromatograph type CHROMPACK CP 9002, using a 50 m long plot fused silica column (0.53 mm ID) with CP-Al_2O_3/KCl as the stationary phase in the temperature programmed mode. The rate was measured using 100 mg catalyst at 15 $cm^3\,min^{-1}$ flow rate, and was calculated in $\mu mol\,s^{-1}\,g_{cat}^{-1}$. The selectivity was calculated according to $(C_i/C_{2+}) \times 100$ for $i = 1$–8. The reaction was characterized by the amount of C_{2+} products in micromoles (in methane equivalents).

3. Results and discussion

The XRD results clearly indicate that most of the Co and Re content of the sample is in the pure metallic state. An amorphous, probably partially oxidized

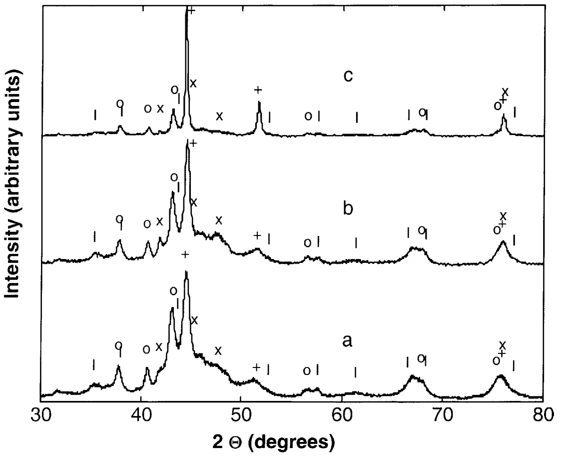

Fig. 1. Room temperature XRD of Re–Co/Al_2O_3 (M) in the as-milled state (a), annealed in H_2 at 350 °C (b) and at 650 °C (c). The measurements were carried out in the diffractometer furnace with uninterrupted H_2 flow. The symbols indicate the peaks of fcc Co (+), hcp Co (×), rhenium (○) and corundum (|).

phase may also be present in the as-milled sample as shown by the broad background peak between about 42° and 50°. This contribution diminishes at 350 °C and completely disappears after annealing at 650 °C. The two metal components are present in separate phases, no peak shift from alloying is observed. Weak and broad lines from corundum are visible, although some of the γ-Al_2O_3 may be amorphous.

The broadening of the XRD lines is a consequence of the very small grain size and the non-uniform lattice strain. Due to the presence of several phases and the overlap of the diffraction lines, the separation of these contributions is not possible. A rough estimate of the grain size of fcc Co was made applying Sherrer's equation to the (1 1 1) and (2 0 0) lines. Grain sizes of 15, 25 and 100 nm were obtained in the as-milled state and after annealing at 450 and 650 °C, respectively (Fig. 1).

The results of the TPR of the Re–Co/Al_2O_3 (M) sample are shown in Fig. 2. The left-hand set of curves reveal that a small amount of reducible oxide is already present in the "as-milled" state (top curve). The reproducible hydrogen uptake at 240 °C is only about 1.7% of the amount of H_2 that would be needed to reduce the bulk from the fully oxidized state. It is likely due to the mixed Re–Co oxide at the skin of the metal particles. Having reduced the sample at 450 °C for 3 h after the first TPR, the amount of hydrogen uptake at 240 °C during the second TPR is diminished (middle curve). This peak is nearly completely vanished when the reduction temperature increased to 650 °C (middle curve on the right side). After full oxidation, both samples take up considerable amount of hydrogen at the same temperature after the third TPR (bottom curves). The main difference is that the location of the TPR peak shifts to a temperature significantly higher than those measured after reduction at both 450 and 650 °C.

It is hard to explain the very small peak at 240 °C. Since after hydrogen treatment the sample was cooled down in hydrogen, stayed overnight in H_2, the TPR started afterwards. This effect is fully reproducible

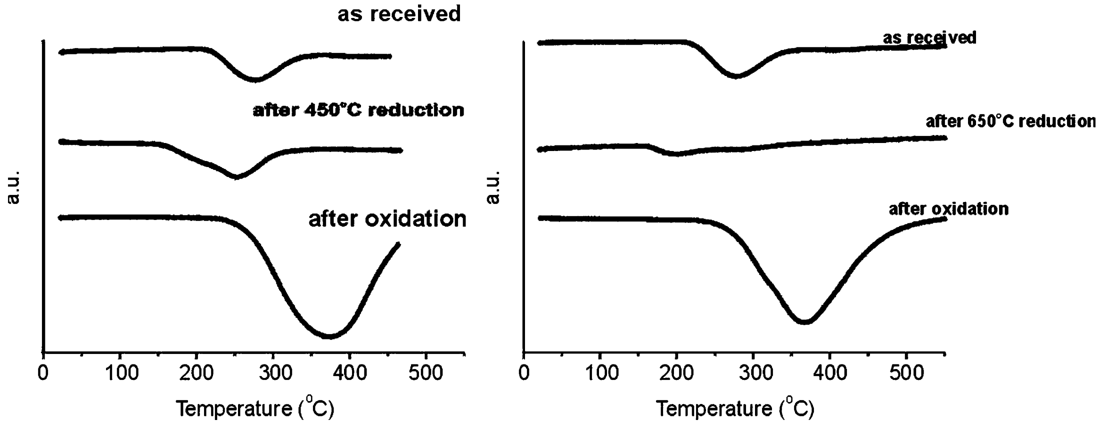

Fig. 2. TPR of the Re–Co/Al_2O_3 (M) samples. Top curves: as received sample; middle curve: after 450 and 650 °C (left and right side, respectively) treatment in hydrogen; bottom curves: after 300 °C oxidation in O_2.

Table 1
TPR and CO chemisorption

Sample	Treatment	H_2 uptake (μmol g^{-1})	CO adsorption (μmol g^{-1})
Re–Co/Al_2O_3 (M)	As-received	194	–
	After TPR H_2/450 °C/3 h	245	0.6
	After O_2/300 °C/2 h	1254	11.0
Re–Co/Al_2O_3 (M)	As-received	210	–
	After TPR H_2/650 °C/3 h	117	4.1
	After O_2/300 °C/2 h	1326	10.5

thus, we have to assume that oxygen occluded after ball milling in the deep layers during overnight, slowly migrates to the outmost layer of the metal particles and forms a less ordered, loosely bound species and reacts easily with hydrogen at lower temperature. Hydrogen treatment at 650 °C decreases the amount of occluded oxygen thus, no significant amount of oxide remains at the surface (right side of Fig. 2). The XRD data indicating substantial grain growth at 650 °C are consistent with the TPR results.

The quantitative TPR data are presented in Table 1. The hydrogen uptake and the CO chemisorption obtained on the as-received and oxidized state agree well as expected. However, when the sample is treated at 650 °C, the CO chemisorption is higher despite the sintering. The most probable explanation is that the surface is better cleaned from oxide moieties.

The rates of CO hydrogenation measured at 10 bar and at 236 °C for both Re–Co/Al_2O_3 (M) and Re–Co/Al_2O_3 (IM) samples are presented in Table 2. The treatment used prior to the reaction is shown in column 2. Direct comparison of the rates is not possible due to the various metal loadings. However, despite the higher metal content of sample Re–Co/Al_2O_3 (M) relative to Re–Co/Al_2O_3 (IM), the CO hydrogenation rate shows a 10-fold increase on Re–Co/Al_2O_3 (IM) relative to Re–Co/Al_2O_3 (M). Moreover, it is also difficult to calculate the turnover frequency because the stoichiometry of CO chemisorption over bimetallic samples is not known. Most likely the mechanically treated samples are the least active catalysts. Even if the rate had been calculated per unit amount of catalysts (per gram of metal), it would have had the smallest values. More informative can be deduced from the α-values (column 5). The most preferred chain growth occurs on Re–Co/NaY (IM) and on the oxidized Re–Co/Al_2O_3 (M) samples (0.97 and 0.94, respectively). In the case of the Re–Co/NaY (IM) it might be explained by the large ratio of chain growth to hydrogenation, as supported by the high value (2.78) of the total olefin/paraffin ($C_n^=/C_n^-$) ratio. For the oxidized Re–Co/Al_2O_3 (M) sample, the explanation should take into consideration the effect of a porous subsurface layer in which chain growth takes place at a high rate, but it can be easily hydrogenated before leaving the porous layer. This is the plausible explanation of the formation of longer alkane chains.

Samples Re–Co/Al_2O_3 (M) and Re–Co/Al_2O_3 (IM) have similar activation energies and selectivity values (Table 2). Regarding the sample prepared by sol/gel

Table 2
Rates, energy of activation, α and olefin/paraffin ratio ($C_n^=/C_n^-$) in the CO hydrogenation over various samples. $H_2/CO = 2$, $T = 236$ °C, pressure = 10 bar

Sample	Treatment	Rate (mol g_{cat}^{-1} s^{-1})	E_{act} (kcal mol^{-1})	α	($C_n^=/C_n^-$)
Re–Co/SiO_2 (SG)	H_2/400 °C/4 h	2.1×10^{-8}	32.5	0.66	0.73
Re–Co/Al_2O_3 (IM)	O_2/300 °C/1 h + H_2/400 °C/2 h	2.5×10^{-6}	33.0	0.83	1.43
Re–Co/NaY (IM)	O_2/300 °C/1 h + H_2/400 °C/2 h	5.7×10^{-7}	32.3	0.97	2.78
Re–Co/Al_2O_3 (M)	H_2/450 °C/4 h	2.5×10^{-7}	35.0	0.82	0.63
Re–Co/Al_2O_3 (M)	H_2/450 °C/2 h + 650 °C/1 h	1.9×10^{-8}	33.4	0.71	0.72
Re–Co/Al_2O_3 (M)	O_2/300 °C/1 h + H_2/450 °C/2 h	1.7×10^{-7}	33.0	0.94	0.46

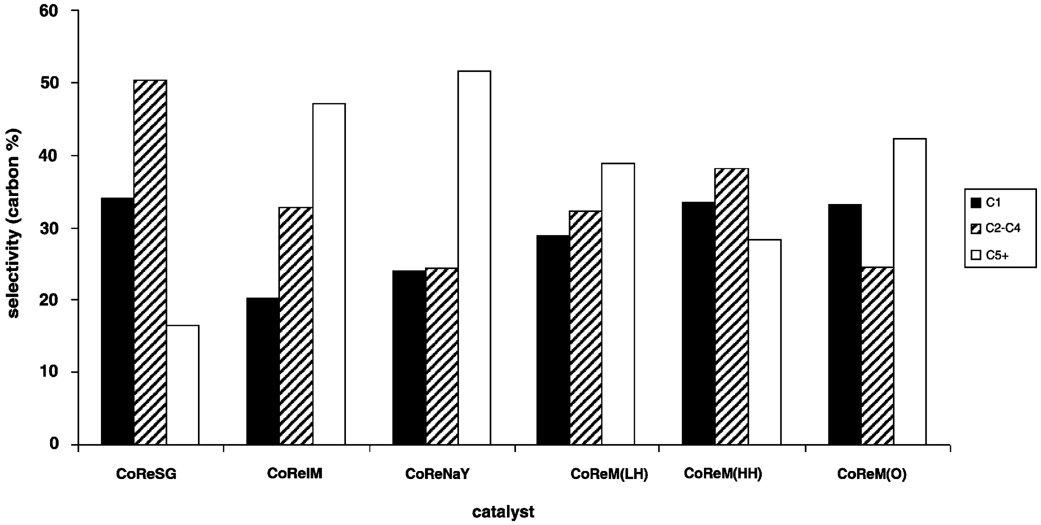

Fig. 3. Comparison of the selectivity values for various samples in CO hydrogenation. (The Re–Co/Al_2O_3 (IM) sample was measured at 218 °C, other conditions, see in text.)

method, the formation of CH_4 is also high and the chain growth is low ($\alpha = 0.66$). This is probably due to the samples being in the amorphous state. The fundamental difference between Re–Co/SiO_2 (SG) and oxidized Re–Co/Al_2O_3 (M) is indicated by the selectivity of short chain hydrocarbon formation. This also points to the porous subsurface layer developed during calcination and reduction in oxidized Re–Co/Al_2O_3 (M), in which the chain growth takes place to a larger extent than on the sol/gel prepared small metal particles.

On the other hand, the rate of the CO hydrogenation is higher on both the Re–Co/Al_2O_3 (M) and Re–Co/Al_2O_3 (IM) samples than on the ReCo/SiO_2 (SG) sample. The CH_4, C_2–C_4 and C_{5+} selectivity values measured on Re–Co/Al_2O_3 (M) and Re–Co/Al_2O_3 (IM) as well as on Re–Co/SiO_2 (SG) and Re–Co/NaY (IM) [5] are shown in Fig. 3. There are marked differences. While Re–Co/SiO_2 (SG) shows an exceptionally high selectivity in the formation of short chain hydrocarbons, the Re–Co/Al_2O_3 (IM) and Re–Co/NaY (IM) samples are active in the C_{5+} hydrocarbon formation. The mechanically treated samples, however, are active both in methane and longer chain hydrocarbon formation.

The values of olefin/paraffin ratio ($C_n^{=}/C_n^{-}$) for hydrocarbons of C_2–C_6 are presented in Fig. 4. The highest ratio is measured on Re–Co/NaY (IM) catalysts. The CH_4 selectivity diminishes while the C_2–C_4 and C_{5+} selectivity increases. This effect is attributed to the rhenium retarding the carbonaceous deposit formation on the catalyst. It is rather intriguing that oxidation followed by reduction resumes the catalytic activity in the CO hydrogenation. The olefin/paraffin ratio measured on the Re–Co/Al_2O_3 (IM) sample (Fig. 4) exhibits a large maximum at C_3 hydrocarbons and the value decreases quickly. It means that the higher olefins can easily be hydrogenated before entering chain growths. On the other hand, both Re–Co/NaY (IM) and Re–Co/SiO_2 (SG) samples show higher olefin/paraffin ratio meaning that hydrogen activation, consequently hydrogenation on the surface species takes place to a lesser extent and thus less hydrogen is available for hydrogenation.

The hydrogenation of CO depends on the activation of C–O bonds. In order to study the cleavage of the C–H bonds, the “two-step” methane conversion was also investigated and the results are presented in Table 3. Prior to the experiments, the samples were treated in H_2 at 450 or at 650 °C (first and second rows, respectively). As the first step, a methane pulse was added to the sample at 450 °C followed by He flush and hydrogenation at 150 °C. The results show that the amount C_{2+} and ethane selectivity increase

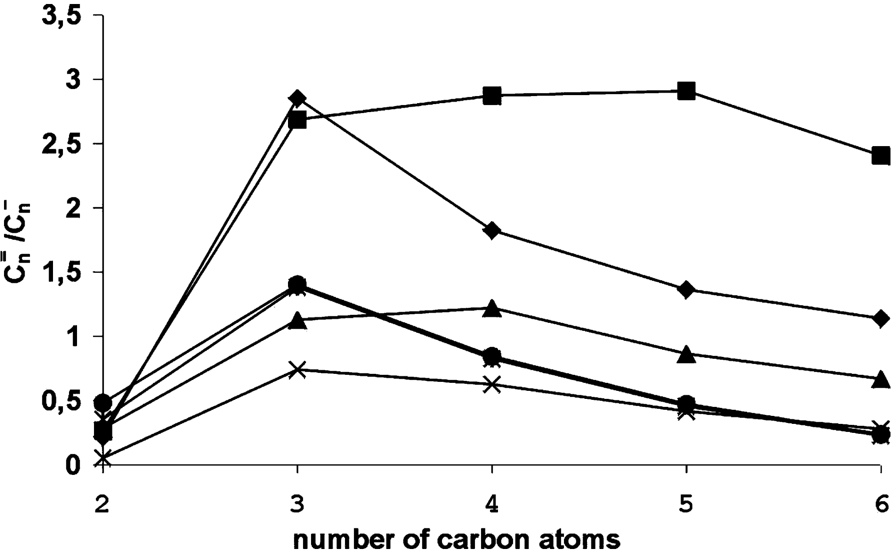

Fig. 4. Olefin/paraffin ratio ($C_n^=/C_n^-$) measured for C_2–C_6 hydrocarbons on the various catalyst samples in the CO hydrogenation. Symbols: (◆) Re–Co/Al_2O_3 (IM); (■) Re–Co/NaY (IM), (●) Re–Co/Al_2O_3 (M, 650), (×) Re–Co/Al_2O_3 (M, ox./red.), (✱) Re–Co/Al_2O_3 (M, 450), (▲) Re–Co/SiO_2 (SG).

when the catalyst was treated with hydrogen at 650 °C. Ethane was formed in 1.7% quantity with 99% selectivity. The activity in methane conversion performed on Re–Co/Al_2O_3 (M) samples is higher when it is compared with the one prepared by incipient wetness Re–Co/Al_2O_3 (IM). While we know that on Re–Co system methane starts adsorbing above 400 °C, it is still surprising that higher hydrocarbons are already removed by hydrogen treatment at 150 °C. Therefore, the activity relationship between Re–Co/Al_2O_3 (M) and Re–Co/Al_2O_3 (IM) is reversed compared to that obtained for the CO hydrogenation. One of the possible explanations is that on larger crystallites the CH_x species as intermediates in the CH_4 decomposition appear to be stable, while the carbon resulting from CO dissociation in the CO hydrogenation reaction forms inactive carbides on the surface, decreasing thereby the number of active sites. On the other hand, over Re–Co/Al_2O_3 (IM) catalyst the carbon species obtained by CO dissociation forms active carbides due to the presence of the oxide species (cobalt oxide, rhenium oxides) that make the metal sites less active for the formation of deactivating carbide species.

Interpretation of the structural and catalytic results is rather difficult. The mechanically treated sample (M) most likely contains disordered Co–Re phases, although we have no evidence from the XRD results on the formation of bimetallic particles. Nevertheless, it is a plausible assumption that crystalline and amorphous phases coexist. As was mentioned earlier, the heat treatment of the samples, e.g. during pretreatment, may affect the crystallinity of the metal particles,

Table 3
Two-step methane conversion over Re–Co/Al_2O_3 (M) and Re–Co/Al_2O_3 (IM) samples

Sample	Treatment in H_2 (°C)	CH_4/admit (μmol)	C_{2+} (μmol)	C_{2+} yield (%)	$S_{C_2H_6}$ (%)	C_2H_6 yield (%)
M	450	22.3	0.21	0.96	75	0.72
M	650	22.3	0.38	1.7	99	1.7
IM[a]	450	22.3	0.13	0.58	2.4	0.01

[a] CH_4 conversion at 250 °C with subsequent H_2 treatment at 250 °C.

i.e. the particle size increases. Major changes in the structure of the mechanically treated samples can be observed during annealing in the temperature range between 450 and 650 °C. The crystal growth reduces the strains and instability caused by the mechanically induced disordering. Annealing quickly eliminates the high Miller-index faces, kinks, edges and corners, that are easily deactivated by cocking and thus the stable activity appears at higher level on the sample treated at higher temperature. This could be the explanation for the higher rate values in the methane activation on sample (M).

However, an inverse relationship is observed in the CO hydrogenation, namely sample (IM) is more active than (M). The possible explanation is the difference in the activation mechanism of the reactant molecule, namely the C–H bond is dissociated in methane activation, while the C–O bond has to be dissociated in the CO hydrogenation. In the latter case, the surface carbon and not the CH_x species should be hydrogenated and this elementary step requires an active site, which has not been annealed and the carbon originated from the CO dissociation, has not been transformed into coke. The above argument is supported by the high activity on the (IM) sample, which, however, shows a poor performance in the methane activation as discussed earlier.

4. Conclusion

The mechanically treated sample (M) contains disordered, probably partly amorphous metal particles, although we have no direct evidence of the formation of bimetallic particles.

Heat treatment of the samples, such as, hydrogenation during pretreatment, affects the crystallinity of the metal particles. Rhenium promotes reduction and maintains the metallic state of cobalt. In the CO hydrogenation there is little difference between samples M and IM apart from the rate, that is considerably higher on the latter sample.

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