

Task 3. Catalyst Characterization

The objective of this task is to obtain characterization data of the prepared catalysts using routine and selected techniques.

A. Deactivation of Noble Metal Promoted Co/Al₂O₃ Catalysts for Fischer-Tropsch

Synthesis

Abstract

Fresh and spent unpromoted and noble metal promoted 15%Co/Al₂O₃ catalysts were analyzed by XANES to provide insight into catalyst deactivation. XANES analysis of spent unpromoted and Ru promoted Co/Al₂O₃ catalysts gave evidence of oxidation of a fraction of the cobalt by water produced during the reaction. From analysis of the pre-edge feature, the oxidized clusters showed evidence of a tetrahedral environment, indicating that either Co₃O₄ and/or Co aluminate was formed. Comparison of XANES derivative spectra to references and LC fitting suggested that some form of Co aluminate species was formed. Because bulk oxidation of Co by water is not permitted thermodynamically under FTS conditions, it is concluded that the smaller clusters interacting with the support and deviating from bulklike behavior undergo oxidation in the presence of water. Promotion with Ru or Pt allowed for the reduction of smaller clusters interacting with the support, yielding more active sites and a higher initial rate of activity. Since these clusters deviated more from the bulk and generated a higher water partial pressure due to enhanced activity, the rate of deactivation was faster for the promoted catalysts.

Introduction

Improving the deactivation rates of Co/Al₂O₃ FTS catalysts has been one of the important challenges facing the development of these catalysts for the conversion of coal and natural gas as alternative resources to crude oil in the production of liquid fuels. In comparison with low cost

iron, cobalt FTS catalysts do not convert water by the water-gas shift reaction. Furthermore, cobalt catalysts are believed to deactivate less and produce higher fractions of linear alkanes than their iron counterparts. A major drawback of cobalt is its high cost, making catalyst replacement during reactor operation undesirable. Therefore, current studies in the literature have focused on improving the deactivation rates of these catalysts.

Our primary goal was to employ a number of characterization techniques to investigate the cause of catalyst deactivation. For example, potential causes include sintering of the cobalt, sintering and segregation of the noble metal promoter, and oxidation of the Co surface. In this investigation, the nature of the deactivation of unpromoted, 0.5% Ru promoted, and 0.5% Pt promoted 15%Co/Al₂O₃ catalysts for FTS was studied using a combination of techniques including XANES, TPR, EXAFS, and XRD. These results are compared with reaction results obtained in CSTRs. From the characterization results, it is concluded that important structural changes took place in the catalysts during reaction which contributed to catalyst deactivation.

Experimental

Catalyst Preparation

Condea Vista Catalox (high purity γ -alumina, 100-200 mesh, 200 m²/g) was used as the support material for the cobalt FTS catalysts. To obtain a cobalt loading of 15%, a multi-step incipient wetness impregnation method was used with a drying step at 353 K in a rotary evaporator following each impregnation. Catalysts with different loadings of ruthenium or platinum promoter were prepared by impregnation (see Table 1) using a ruthenium nitrosylnitrate solution or tetraammineplatinum (II) nitrate, respectively. After promoter addition, the catalysts were dried in a rotary evaporator at 353K again and calcined at 673K for 4hrs.

BET Measurements

BET measurements for the catalysts were conducted to determine the loss of surface area with loading of the metal. These measurements were conducted using a Micromeritics Tri-Star system. Prior to the measurement, samples were slowly ramped to 433K and evacuated for 4hrs to approximately 50mTorr. Results of physisorption measurements are shown in Table 1.

Hydrogen Chemisorption with Pulse Reoxidation

Hydrogen chemisorption measurements were performed using a Zeton Altamira AMI-200 unit, which incorporates a thermal conductivity detector (TCD). The sample weight was always 0.220 g. The catalyst was activated at 623K for 10hrs using a flow of pure hydrogen and then cooled under flowing hydrogen to 373K. The sample was held at 373 K under flowing Ar to prevent physisorption of weakly bound species prior to increasing the temperature slowly to the activation temperature. At that temperature, the catalyst was held under flowing Ar to desorb the remaining chemisorbed hydrogen so that the TCD signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibrated hydrogen pulses. Prior to experiments, the sample loop was calibrated with pulses of N₂ in helium flow and compared against a calibration line produced from gas tight syringe injections of N₂ under helium flow.

After TPD of H₂, the sample was reoxidized at the activation temperature by injecting pulses of pure O₂ in helium referenced to helium gas. After oxidation of the cobalt metal clusters, the number of moles of O₂ consumed was determined, and the percent reducibility calculated assuming that the Co⁰ reoxidized to Co₃O₄. Results are summarized in Table 2.

Temperature Programmed Reduction

Temperature programmed reduction (TPR) profiles of fresh catalyst samples were obtained using a Zeton Altamira AMI-200 unit. Calcined fresh samples were first heated and purged in flowing Ar to remove traces of water. TPR was performed using 30 cc/min 10% H_2 /Ar mixture referenced to Ar. The ramp was 5K/min from 303K to 623K, and the sample was held at 623K for 30 min.

X-ray Diffraction

X-ray diffraction measurements were conducted at the National Synchrotron Light Source at Brookhaven National Laboratory, beamline X10b. The experimental apparatus consisted of a six circle Huber diffractometer, ion chambers, and Bicorn scintillation detectors. The scanning step was 0.020° and each point was scanned for approximately 13.8 s.

EXAFS/XANES

XAFS measurements on reference samples, calcined catalysts, reduced/passivated fresh catalysts, and used catalysts were obtained at the National Synchrotron Light Source at Brookhaven National Laboratory, Upton, NY, using beamline X-18b equipped with a Si (111) channel cut monochromator. The crystal was detuned to prevent glitches from the third harmonic. The X-ray ring at the NSLS has a flux of $1E10$ photons per sec at 100 mA and 2.5 GeV, and the energy range capability was 5.8-40 keV. XAFS data were recorded near the K edge of Co. The XAFS spectra were recorded at liquid nitrogen temperatures in a cell to minimize the contribution from the dynamic Debye Waller factor. Several scans were taken and the average obtained by adding the scans. The pre-edge background was subtracted by using power series curves and then the post-edge background was removed using a cubic spline routine. The spectra were normalized by dividing by the height of the absorption edge. XANES spectra were

compared after normalization, and resulting normalized spectra were fitted using WinXAS 97 [1]. References used for XANES measurements included the Co foil, Co_3O_4 , CoO , CoAl_2O_4 . For EXAFS, Chi-data were obtained by truncating the normalized spectra 50 eV after the edge jump and background subtracting with splines. To emphasize the Co-Co interaction, the Chi-data were k^3 -weighted. To obtain qualitative information on the Co metal cluster size, Fourier transform magnitudes of the results in k-space were determined and compared to the Co foil.

Results and Discussion

Figure 1 shows TPR of the unpromoted $\text{Co}/\text{Al}_2\text{O}_3$ catalyst in comparison with TPR spectra for Ru promoted catalysts with increasing loadings of ruthenium, and the 0.5% Pt promoted catalyst. Note that in the TPR, the temperature was not ramped high enough to observe the decomposition of cobalt aluminate species, which has been shown to occur above 1073 K with up to 30% loading of cobalt [2]. The broad peak on the unpromoted catalyst (700 to 1000 K) is attributed to the reduction of CoO to Co^0 , and the different shoulders to varying degrees of interaction with the support as a function of the cluster size, in agreement with a previous XRD/TPR study [3]. In that work, XRD was scanned after reduction of the first peak in TPR. It was clearly observed that the 31.2° and 59.4° peaks for Co_3O_4 disappeared, while the 42.4° and 61.3° peaks for CoO appeared. The smallest CoO clusters, with the strongest interaction with the support, therefore, likely reduce to produce the 950 K shoulder. The addition of Ru caused the peaks to shift markedly to lower temperatures, presumably due to spillover of H_2 from the reduced promoter to reduce the Co oxide species, in agreement with an earlier study [4]. Of particular importance, peaks that are attributed to $\text{CoO}-\text{Al}_2\text{O}_3$ support interaction are reduced at lower temperatures with increasing Ru loading, or with addition of Pt. Results of H_2 chemisorption by TPD in Table 2 indicate that the number of surface sites increases with addition

of either Ru or Pt promoter. By performing pulse reoxidation, it is clear that the remarkable gain in site density is mainly due to an enhancement in the reducibility of the Co^0 cluster, and not to improvements in the actual dispersion (cluster size) [5]. However, addition of Ru or Pt causes a slight contraction in the average cluster size. This is reasonable, because the comparison was conducted in samples treated at the same reduction temperature of 623 K, and the addition of Ru or Pt causes a fraction of the smaller CoO clusters interacting with the support to be reduced at this temperature, resulting in a slightly smaller average cluster.

X-ray diffraction (XRD) patterns for the calcined fresh unpromoted and Ru promoted catalysts are shown in Figure 2. The peaks at 46.1° and 66.5° correspond to the $\gamma\text{-Al}_2\text{O}_3$ support, while the other peaks correspond to the different crystal planes of Co_3O_4 [3]. From line broadening analysis using Winfit for the peak at 36.8° corresponding to (311), it was determined that the average Co_3O_4 cluster size after calcination was approximately 10.6 nm (unpromoted) and 10.3 nm (0.5% Ru promoted) corresponding to 7.95 nm and 7.73 nm when reduced to the metal, respectively. This is a reasonable result in comparison to the results of hydrogen chemisorption. XRD on the used catalysts was also performed and the resulting spectra were very complex. The benefit of using synchrotron radiation is that the intensity of X-rays decreases the signal to noise ratio considerably, allowing for the analysis of species which would otherwise be below detectable limits. Interestingly, the series of 16 complex peaks between 30° and 80° were identical for both the promoted and unpromoted spent catalysts. Although peaks for Co metal were clearly identified at 41.7° and 44.8° in addition to the support peaks at 46.1° and 66.5° , the identification of the remaining peaks continues.

XANES analysis was conducted for the reference compounds CoO, Co₃O₄, CoAl₂O₄, and the Co foil and for the calcined (c), freshly reduced/passivated (rp) and used (us) unpromoted (ZYQ000) 0.5% Ru promoted (ZYQ050), and 0.5% Pt promoted (ZYQ036) catalysts. The normalized and derivative spectra are displayed in Figures 3 and 4. The XANES of the K-edges of some Co compounds contain a pre-edge feature useful for characterizing the structure, as it appears for tetrahedral cobalt environments but is forbidden (in reality appears much weaker) for octahedral environments [6]. The peak represents the 1s to 3d transition and the probability for the scattering event depends on the symmetry and the number of available states in the 3d shell. Therefore, the intensities follow the order CoAl₂O₄ > Co₃O₄ > CoO, as the cobalt atoms in CoAl₂O₄ are in a tetrahedral environment, the cobalt atoms in the spinel structure of Co₃O₄ are in a mixed environment (one Co atom in a tetrahedral environment, while the other two are in octahedral), and the cobalt atoms in CoO are in an octahedral environment [6].

The calcined catalysts, in agreement with XRD, clearly display Co₃O₄ as the major species present on the support. After performing a linear combination (LC) fitting of the XANES for the calcined catalysts using WinXAS 97, the result was a 100% contribution from Co₃O₄. Interestingly, in the derivative spectra, the calcined catalysts have a pre-edge feature similar to Co₃O₄, while the freshly reduced/passivated catalysts have a smaller pre-edge feature similar to that of CoO. Also, for the reduced/passivated catalysts, the white line is very similar in shape to that of CoO. This is in agreement with the conclusion from TPR. After reduction at 623K, the first peak in TPR, assigned to reduction of Co₃O₄, is nearly completely reduced, while the CoO peak is only partially reduced, due to interaction of this species with the support. For the promoted catalysts, the extent of reduction is 20% and 30% higher for Ru and Pt promoted catalysts, respectively, than for the unpromoted sample. It is reasonable that, after passivation, the XANES features of the fresh

catalysts will most resemble the spectra of CoO. As expected, after performing a linear combination (LC) fitting of the XANES with WinXAS 97, the CoO was found to contribute to 93.6%, 99.2%, and 48.2% of the XANES for unpromoted, Ru promoted, and Pt promoted catalysts, respectively, as shown in Table 3.

Interestingly, for the used catalysts, the spectra appear to be very similar for both the promoted and unpromoted catalysts. It is clear that the resulting complex spectra for the used catalysts represent a combination of superimposed spectra of different species rather than one dominating contribution. First, in considering the pre-edge feature, there appears to be a feature indicating the presence of a tetrahedral environment superimposed over the broad signal of the metal (octahedral environment). The intensity of the feature suggests the presence of Co_3O_4 or CoAl_2O_4 over that of CoO in the used catalysts. This assignment is further strengthened by considering the white line. Clearly, the position of the white line, as viewed in the derivative spectra, matches more closely the spectra of either Co_3O_4 or CoAl_2O_4 . Comparison of the spectra for the used catalysts with the calcined, where only Co_3O_4 is present, suggests the cobalt aluminate formation. This is clear, because the third major peak is higher in the calcined catalyst, indicating Co_3O_4 , while the first peak dominates the spectra of the used catalysts, suggesting a species with similar oxidation state properties to CoAl_2O_4 .

To further strengthen this assignment, three separate fittings were performed on the spent catalysts, as depicted in Table 3 for the catalysts ZYQ000us, ZYQ050us, and ZYQ036us. In fitting #1, the XANES spectra were fitted with Co^0 , Co_3O_4 , and CoO, while the CoAl_2O_4 was left out of the fitting. The resulting residual was calculated to be 2.00, 1.43, and 1.6 for the unpromoted, Ru-promoted, and Pt-promoted catalysts, respectively. In fitting #2, however, the spectra were fitted with Co^0 , CoAl_2O_4 , and CoO, while the Co_3O_4 was removed from the fitting. In that case, the

residuals for all three spectra decreased, indicating a much better fitting, with the values of 1.49, 1.29, and 1.54, respectively. In fitting #3, both the Co_3O_4 and CoAl_2O_4 were left in the fitting procedure, and the results for the unpromoted and Ru-promoted catalysts showed no further improvement, indicating that the CoAl_2O_4 was a better fit. The Pt-promoted catalyst displayed some further improvement with both species present in the fitting. However, the cobalt aluminate percentage was higher. Note that samples of the used catalysts were taken after reactor shutdown, in the wax, at different times on stream and after varying stages of deactivation. These catalysts were also used in kinetics testing, and the aim of this work was to identify a potential species responsible for deactivation. Further studies will be carried out to obtain better quantitative information on the evolution of cobalt oxide/aluminate formation. Nevertheless, the results suggest that the H_2O produced from the FTS reaction may have an oxidizing effect on the small cobalt clusters, which do not exhibit the same properties as the bulk metal. Note that very large $P_{\text{H}_2\text{O}} / P_{\text{H}_2}$ ratios (>50) are needed to oxidize bulk Co metal [7], and these ratios will not be encountered under normal FTS conditions. It is suggested here that the support interaction promotes the deviation of small clusters from bulk-like behavior. Therefore, it is clearly of interest to continue to investigate the effect of increasing the cluster size for Al_2O_3 supported Co catalysts and to determine the impact of the cluster size on the deactivation rate of the catalyst.

To assess the change in the Co metal cluster size, EXAFS was conducted on the freshly reduced/passivated and used catalysts. The k^3 -weighted Fourier Transform magnitudes are displayed in Figure 5 in reference to the Co foil, which displays a coordination of 12. Interestingly, both the fresh reduced/passivated catalysts (promoted and unpromoted) displayed similar Fourier Transform magnitudes, indicating a similar cluster size. After reaction, the relative cluster size was higher for the Ru and Pt promoted catalysts than the unpromoted.

Therefore, two possibilities are likely – either sintering of the clusters occurred during reaction, or the smaller clusters reoxidized to some species during reaction, leaving a higher intensity for Co-Co in the k^3 weighted Fourier Transform for the used catalyst, indicating a larger average Co metal cluster size. The Ru and Pt promoted catalyst exhibited a larger Co^0 size.

Reaction testing in the CSTR revealed that higher conversions and, therefore, increasing $P_{\text{H}_2\text{O}}$, resulted in a higher catalyst deactivation rate. In a previous investigation for a 0.5% Pt promoted 15%Co/ Al_2O_3 catalyst, $P_{\text{H}_2\text{O}} > 28\%$ resulted in drastic irreversible deactivation to the catalyst [8]. In this investigation, the catalysts were run at the same space velocity on a per gram catalyst basis, but the number of active sites was higher for the Ru and Pt promoted catalysts, resulting in higher initial activity for both catalysts. In agreement with our previous findings, the more active catalysts displayed a higher rate of deactivation, as shown in Figure 6. For the unpromoted catalyst, the CO conversion decreased by 18% of the initial activity after 85 h, it remained stable after that. In contrast, the CO conversion decreased by 42% of the initial value after 1000 h for the Ru-promoted catalyst, and 43% after 620 h for the Pt-promoted catalyst. The influence of pressure and temperature on FTS has been well-documented. Studies on Co catalysts have shown that while increasing temperature results in a shift of products to lower carbon numbers, increasing total pressure shifts product selectivities to heavier products. The process conditions used in this work were $T=493\text{K}$, $P=275$ psig, $SV=5$ SL/hg cat.

In a previous investigation of Co/ Al_2O_3 unpromoted and Re promoted Co/ Al_2O_3 catalysts, Schanke et al. [9] showed by gravimetric analysis and XPS that reoxidation occurs when water is introduced after reduction of the catalyst. The extent of reoxidation was found to be dependent on the partial pressure of water and the composition of the feed mixture. At atmospheric pressure, for

example, without H₂ in the feed, complete surface reoxidation was found to occur after short exposure times, while only slight indications of reoxidation were seen under H₂. However, at high pressure conditions of 20 bar, which is comparable to the pressure in an FTS reactor, reoxidation occurred to a higher extent. Interestingly, the Re promoted catalyst was found to be more susceptible to deactivation than the unpromoted. The authors noted that bulk cobalt metal will not reoxidize in H₂O/H₂ mixtures, as predicted by thermodynamic calculations. However, the influence of the support on metal and metal oxide clusters causes deviations from bulk behavior. Re, Pt, and Ru catalyze the reduction of smaller clusters which will not be reduced on the unpromoted catalyst. This is indicated by the contraction of average cluster size as determined by H₂ chemisorption. In addition to Ru and Pt catalysts, we have obtained similar contraction of cluster size with Re promotion, also. It is suggested that these smaller clusters deviate more strongly from bulklike behavior and will be more susceptible to reoxidation. Therefore, the faster deactivation rate observed for the Ru and Pt promoted catalysts in this work can be likely attributed to two factors. First, the increased activity due to more active sites will yield a higher water partial pressure in the reactor. Secondly, with a higher fraction of smaller clusters after reduction, the promoted catalyst is more susceptible to reoxidation.

A recent study [3] reported on the effect of water partial pressure on the reducibility of Co for a Ru-promoted cobalt catalyst. Increasing the water partial pressure was found to increase the reduction temperature of the second peak of the TPR, which they assigned to the reduction of well dispersed Co species that strongly interact with the support. Furthermore, adding water decreased the overall degree of reduction. This latter result suggests that water promotes interactions between Co oxide species and the γ -Al₂O₃ support, so that irreducible cobalt aluminate was formed. Therefore, in the case of catalyst deactivation, one cannot rule out the possibility of cobalt aluminate

formation. It is conceivable that, once oxidized by water, the well dispersed clusters, for which there exists a strong interaction with the support, may diffuse as ions into the support in the presence of water produced from reaction, and form some type of irreducible tetrahedral cobalt aluminate species.

Conclusions

XANES analysis of spent unpromoted and Ru or Pt promoted 15% loaded Co/Al₂O₃ catalysts gave evidence of oxidation of a fraction of the catalyst from water produced during the reaction. From analysis of the pre-edge feature and the XANES derivative spectra, the oxidized clusters showed evidence of a tetrahedral environment, indicating that either Co₃O₄ or Co aluminate was formed. The two are not easily distinguished by either XRD or XANES but comparison of XANES spectra of spent and calcined catalysts and linear combination fitting against reference spectra suggested Co aluminate formation. Because bulk oxidation of Co is not permitted by water by thermodynamics under FTS conditions, the conclusion was that only the very small clusters interacting with the support and deviating from bulk-like behavior oxidized in the presence of water produced during the reaction. TPR and hydrogen chemisorption results indicated that promoting the catalyst with Ru or Pt allowed for the reduction to metal of a fraction of smaller CoO clusters which were not reduced for the unpromoted catalyst. Therefore, the resulting smaller metal clusters deviated even more from the bulk; therefore, the promoted catalyst was more susceptible to reoxidation, as indicated by reaction testing. While the catalyst displayed higher initial activity due to the presence of a greater number of active sites from enhanced reducibility, the deactivation rates for these catalysts were faster than the unpromoted catalyst.

Acknowledgments

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Table 1			
BET Measurements			
Sample ID	Catalyst Description	BET Surface Area (m ² /g)	Average Pore (nm)
ZYQ000	15%Co/Al ₂ O ₃	157.7	4.2
ZYQ036	0.5%Pt-15%Co/Al ₂ O ₃	161.6	4.1
ZYQ050	0.5%Ru-15%Co/Al ₂ O ₃	161.0	3.2
ZYQ054	0.2%Ru-15%Co/Al ₂ O ₃	153.8	4.0
ZYQ055	1.0%Ru-15%Co/Al ₂ O ₃	159.1	3.1

<i>Table 2</i>								
<i>Sample #</i>	<i>Sample Description</i>	<i>$\mu\text{mol H}_2$ desorbed</i>	<i>Uncorr %D</i>	<i>Uncorr D (nm)</i>	<i>$\mu\text{mol O}_2$ pulsed per g</i>	<i>% Red</i>	<i>Actual %D</i>	<i>Actual D (nm)</i>
ZYQ000	15%Co/Al ₂ O ₃	66.9	5.3	19.6	509	30	17.5	5.9
ZYQ036	0.5%Pt-15%Co/Al ₂ O ₃	140.6	9.3	11.0	1024	60	18.4	5.6
ZYQ050	0.5%Ru-15%Co/Al ₂ O ₃	115.5	9.7	11.4	823	50	18.2	5.7

Table 3
XANES LC Fits

Sample ID	Sample Name	Co ⁰	E ₀ shift (eV)	Co ₃ O ₄	E ₀ shift (eV)	CoO	E ₀ shift (eV)	CoAl ₂ O ₄	E ₀ shift (eV)	Res
ZYQ000c	15%Co/Al ₂ O ₃ calcined	ND	ND	100	1.11+/-0.002	ND	ND	ND	ND	-
ZYQ000rp	15%Co/Al ₂ O ₃ reduced/passivated	6.4	-0.672 +/-0.072	ND	ND	93.6	1.189 +/-0.003	ND	ND	2.19
ZYQ000us fitting #1	15%Co/Al ₂ O ₃ used	36.8	0.045 +/-0.007	24.5	0.174 +/-0.093	38.7	-0.095 +/-0.054	not included	not included	2.00
ZYQ000us fitting #2	15%Co/Al ₂ O ₃ used	38.3	-0.105 +/-0.070	not included	not included	31.9	-0.086 +/-0.058	29.8	0.813 +/-0.055	1.49
ZYQ000us fitting #3	15%Co/Al ₂ O ₃ used	38.3	-0.105 +/-0.070	ND	ND	31.9	-0.086 +/-0.058	29.8	0.813 +/-0.055	1.49
ZYQ050c	0.5%Ru-15%Co/Al ₂ O ₃ cal	ND	ND	100	1.03+/-0.002	ND	ND	ND	ND	-
ZYQ050rp	0.5%Ru-15%Co/Al ₂ O ₃ reduced/passivated	0.8	-0.385 +/-0.001	ND	ND	99.2	1.031 +/-0.003	ND	ND	2.60
ZYQ050us fitting #1	0.5%Ru-15%Co/Al ₂ O ₃ used	52.1	-0.235 +/-0.087	12.2	0.577 +/-0.298	35.7	-0.128 +/-0.093	not included	not included	1.43
ZYQ050us fitting #2	0.5%Ru-15%Co/Al ₂ O ₃ used	53.2	-0.315 +/-0.083	not included	not included	33.2	-0.094 +/-0.011	13.5	1.32 +/-0.189	1.29
ZYQ050us fitting #3	0.5%Ru-15%Co/Al ₂ O ₃ used	53.2	-0.315 +/-0.083	ND	ND	33.2	-0.094 +/-0.011	13.5	1.32 +/-0.189	1.29
ZYQ036rp	0.5%Pt-15%Co/Al ₂ O ₃ reduced/passivated	32.3	-0.287 +/-0.052	19.5	0.876 +/-0.067	48.2	1.375 +/-0.026	ND	ND	1.81
ZYQ036us fitting #1	0.5%Pt-15%Co/Al ₂ O ₃ used	67.2	-0.153 +/-0.007	11.1	1.035 +/-0.034	21.7	-1.45 +/-0.015	not included	not included	1.60
ZYQ036us fitting #2	0.5%Pt-15%Co/Al ₂ O ₃ used	69.3	-0.189 +/-0.007	not included	not included	19.9	-1.38 +/-0.016	10.9	1.65 +/-0.026	1.54
ZYQ036us fitting #3	0.5%Pt-15%Co/Al ₂ O ₃ used	64.9	-0.238 +/-0.008	6.9	-0.251 +/-0.071	20.8	-1.873 +/-0.017	7.4	3.718 +/-0.043	1.49

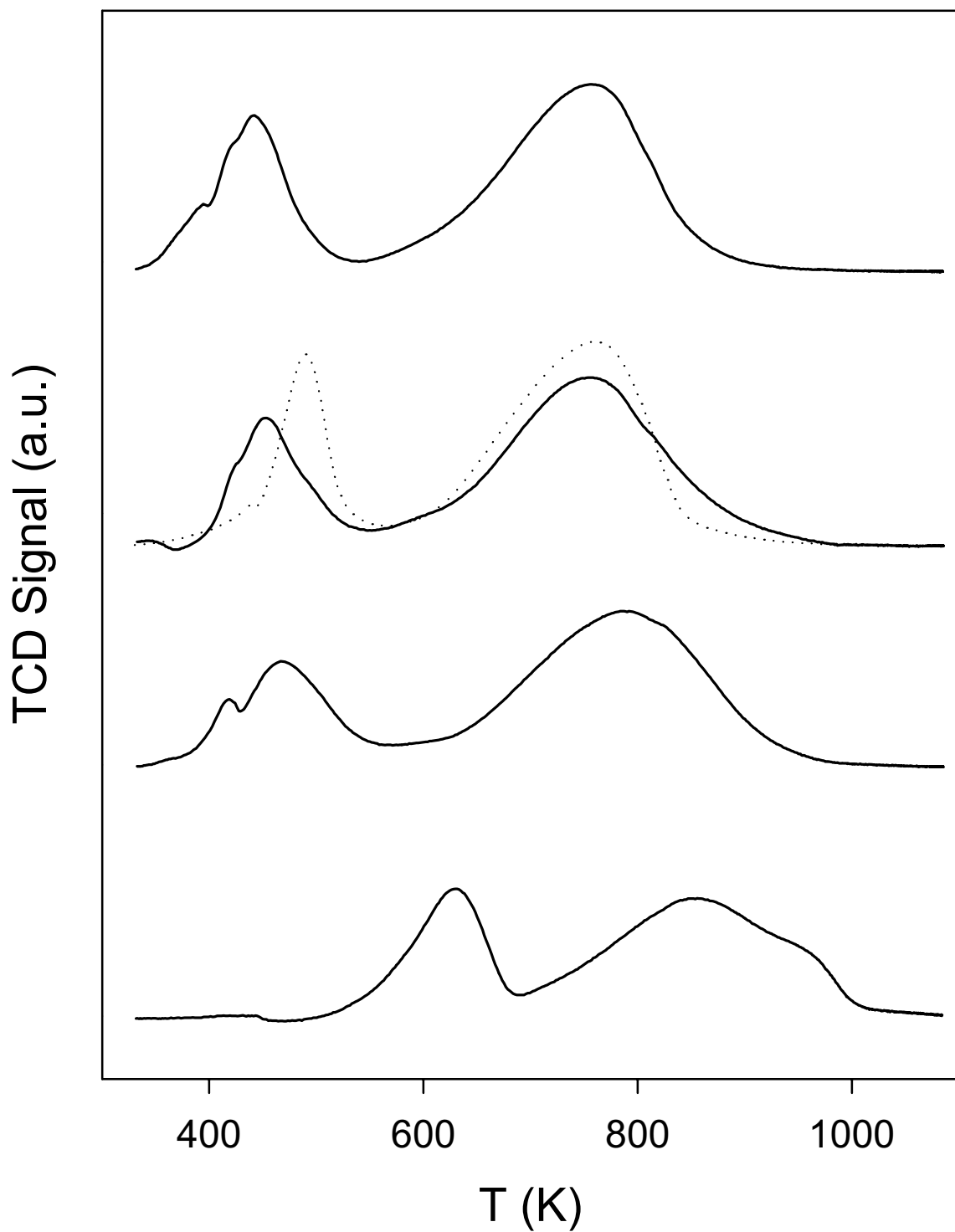


Figure 1. Comparative TPR spectra of unpromoted (bottom) 15%CO/Al₂O₃ catalyst with those promoted with (moving up, solid) 0.2%, 0.5% and 1.0% Ru and 0.5% Pt (dotted).

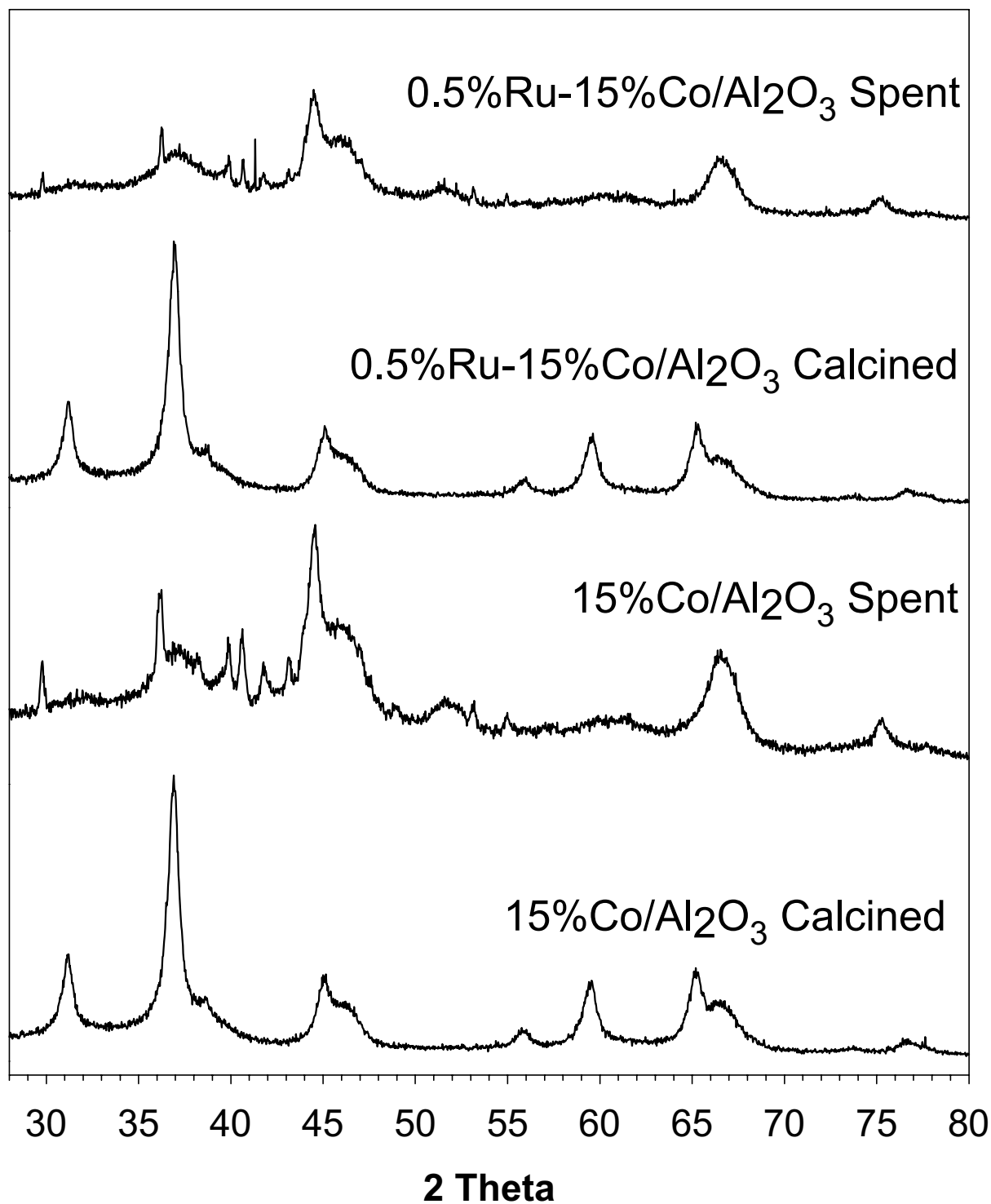


Figure 2. XRD patterns for calcined and spent Ru-promoted and unpromoted 15% loaded Co/Al₂O₃ catalysts.

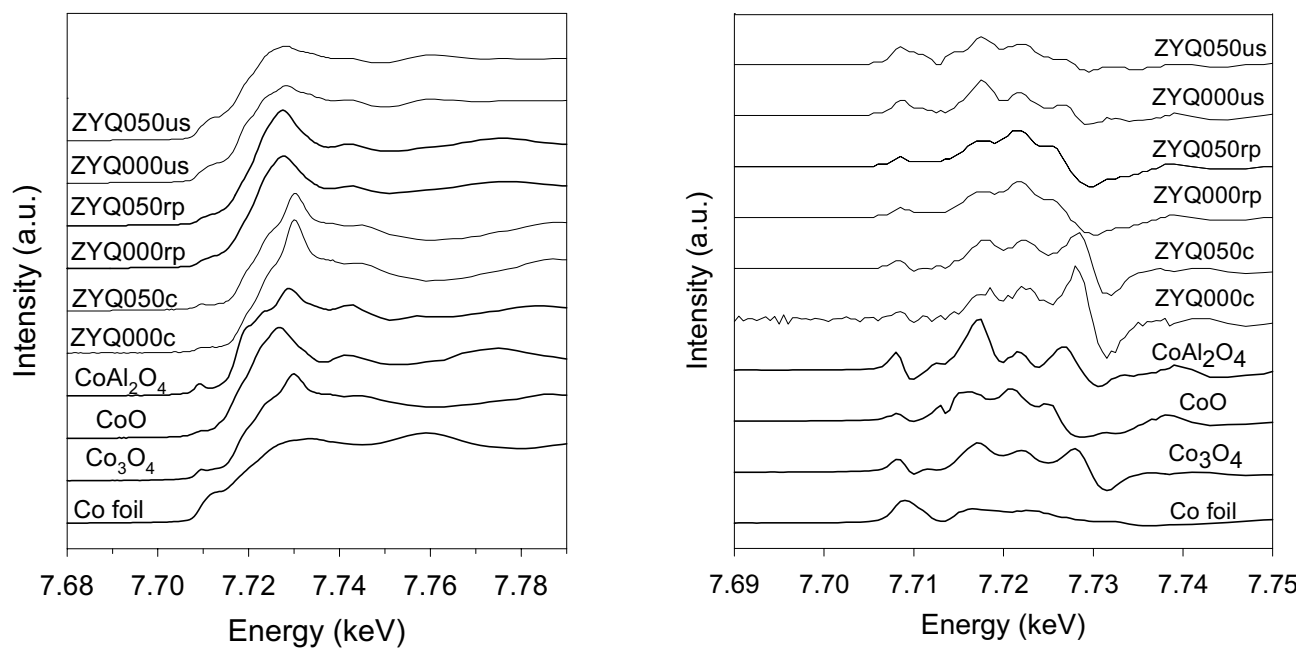


Figure 3. (left) Normalized XANES and (right) XANES derivative profiles for references, calcined, freshly reduced/passivated catalysts and used catalysts. Comparison of Ru promoted and unpromoted FTS catalysts.

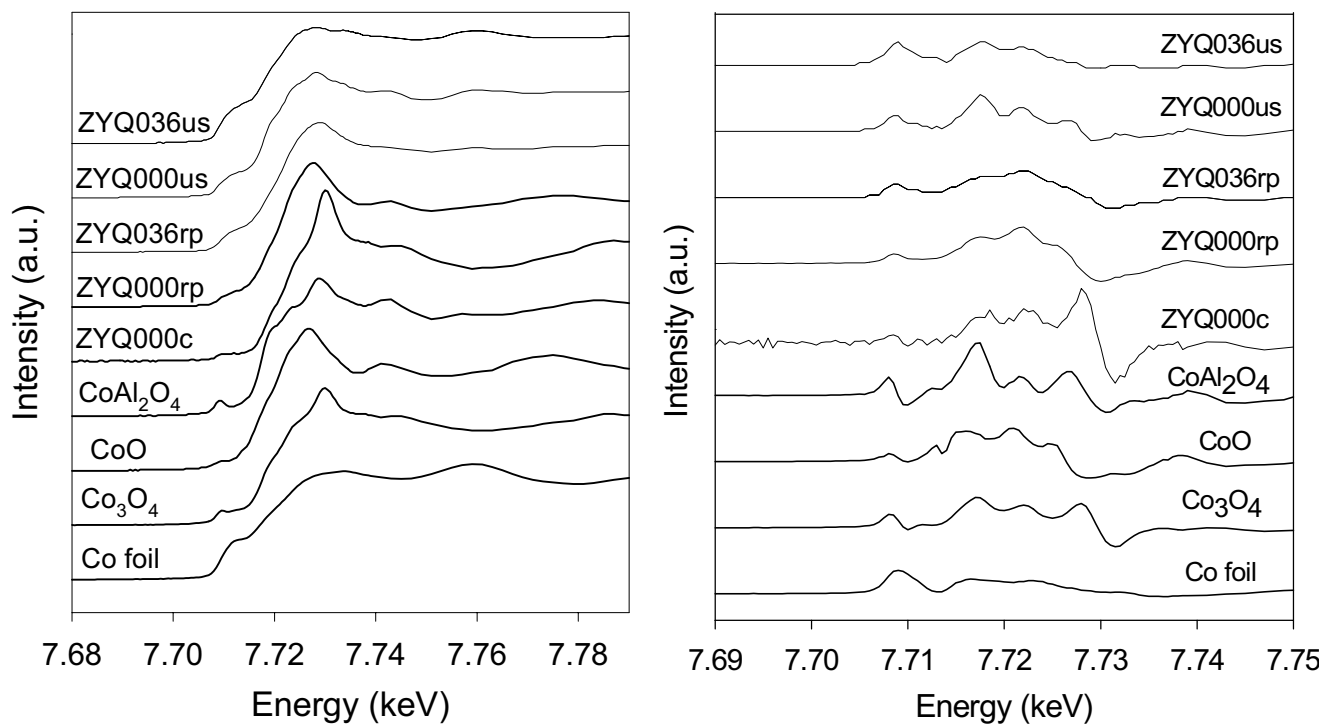


Figure 4. (left) Normalized XANES and (right) XANES derivative profiles for references, calcined, freshly reduced/passivated catalysts and used catalysts. Comparison of Pt promoted and unpromoted FTS catalysts.

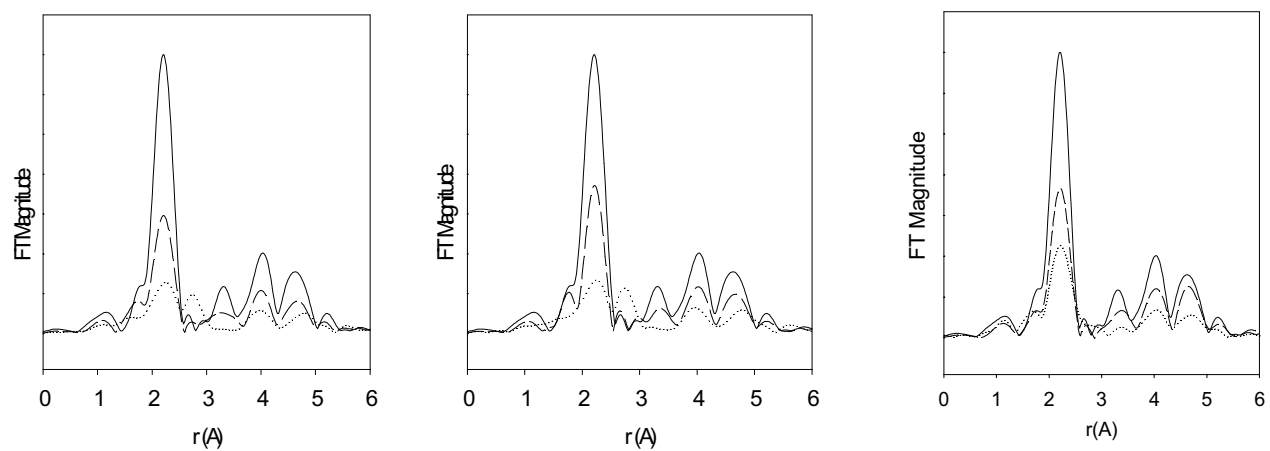


Figure 5. k^3 Weighted Fourier transform magnitudes of Co foil (solid), fresh reduced/passivated catalyst (dotted), and used (dashed) catalyst for (left) unpromoted, (center) 0.5% Ru promoted and (right) 0.5% Pt promoted catalysts.

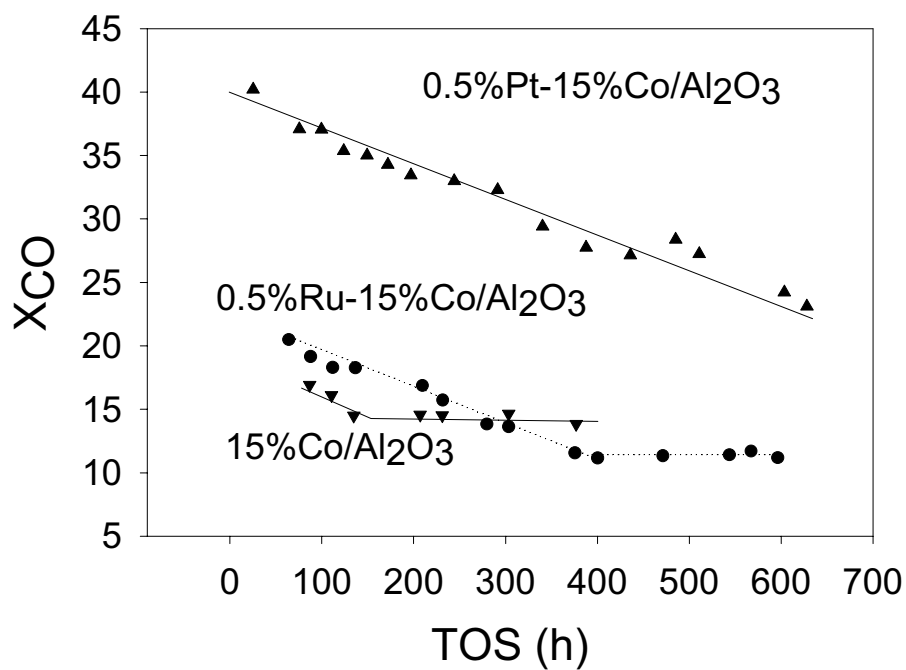


Figure 6. Deactivation of Ru and Pt promoted and unpromoted 15% Co/Al₂O₃ catalysts in a CSTR.