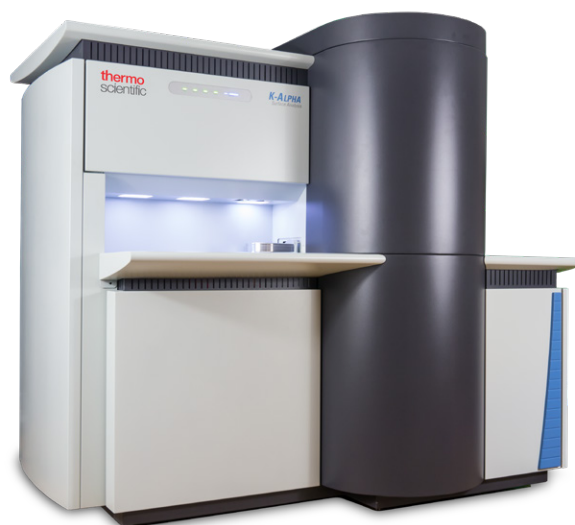APPLICATION NOTE

Investigating the oxidation of a cobalt-based catalyst using X-ray photoelectron spectroscopy

The Thermo Scientific™ K-Alpha™ X-ray Photoelectron Spectroscopy (XPS) System was used to investigate the surface chemical change between a fresh γ-alumina supported Co(Ni) MoS hydrodesulfurization catalyst and the same catalyst after exposure to air. By using XPS, identification and quantification of chemical differences between the two samples were possible.

Introduction

Chemical state determination and quantification are of critical importance when understanding the performance of catalysts. Metal-based catalysts are typically used for redox reactions, and so careful control of the metal oxidation state is required to ensure that the catalyst performs successfully. The surface of the material is where the reaction occurs; thus a method of measuring the surface chemistry of the catalyst is required. XPS is an excellent technique for this type of characterization. Samples are analyzed under vacuum, and so surface changes during the analysis are kept to a minimum. XPS is an extremely surface-sensitive technique, too. Spectra result from within the top 10 nm of the surface, which allows XPS to focus on the crucial surface area. Finally, XPS can identify and quantify both elemental compositions and the chemical states of the elements detected.

The high performance of the Thermo Scientific™ K-Alpha™ X-ray Photoelectron Spectroscopy (XPS) System enables researchers to use XPS to quickly and clearly determine the composition and chemical states of the surfaces of catalyst samples. In this application note, we describe how the K-Alpha XPS System was used to analyze a γ-alumina supported Co(Ni)MoS catalyst to obtain chemical state information from both a fresh and air exposed sample and determine the type and level of chemical change the catalyst underwent when exposed to air.

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Method

The catalyst pellet was removed from its storage under hexane and mounted directly onto double-sided copper tape, which had been adhered to the sample platter. The sample block was then immediately loaded into the fast-entry load-lock and automatically pumped down and transferred into the analysis chamber. The pellet was analyzed for elemental and chemical state information. Once this analysis was complete, the sample was transferred out of the system and exposed to air at atmospheric pressure for three minutes. The sample was then pumped down and transferred back into the analysis chamber. The subsequent XPS analysis was compared with the original results to determine the level of oxidation of the sample surface following exposure to air.
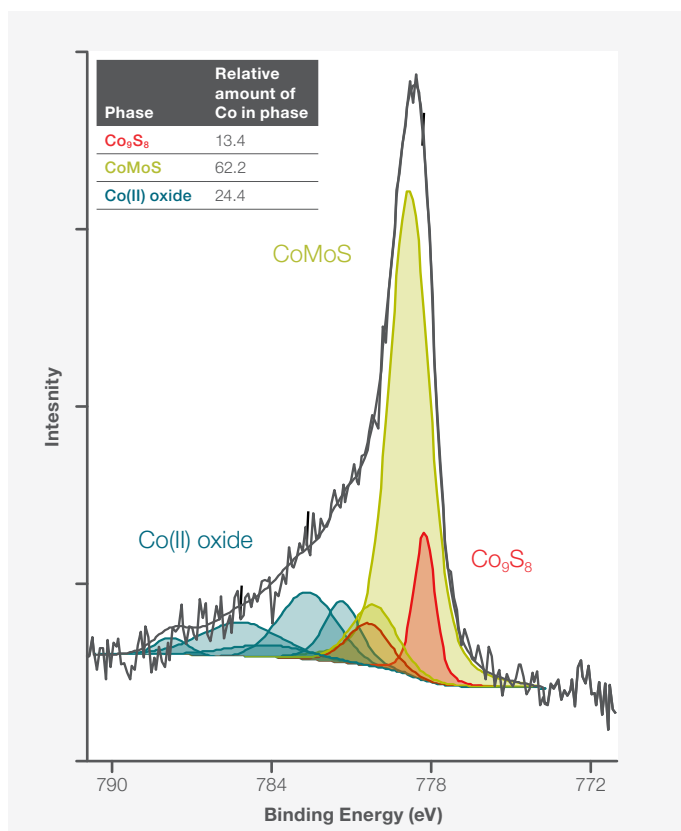
Results

The $Co2p_{3/2}$ spectra recorded on fresh and aged catalysts are shown in Figures 1 and 2, respectively. The different phases of cobalt were quantified using the integrated peak fitting software in the Avantage data system according to Reference 1.

The spectrum was fitted using a multicomponent fit assuming Co_9S_8, CoMoS and Co(II) oxide phases. No significant oxidation was observed when transferring the sample from container to the K-Alpha XPS System, confirming that the sample had the expected composition.

More oxidation was observed after exposure to air, leading to an increase in the relative amounts of Co(II) oxide and Co_9S_8 at the surface and a decrease in the relative amount of CoMoS.

Phase	Relative amount of Co in phase
Co_9S_8	13.4
CoMoS	62.2
Co(II) oxide	24.4

Figure 1: $Co2p_{3/2}$ spectrum of fresh catalyst.

Phase	Relative amount of Co in phase
Co_9S_8	19.0
CoMoS	43.0
Co(II) oxide	38.0

Figure 2: $Co2p_{3/2}$ spectrum of aged catalyst.

Phase	Relative amount of Mo in phase
Mo(II) sulfide	87.2
Mo(IV) oxide	4.7
Mo(VI) oxide	8.1

Figure 3: Mo3d spectrum of fresh catalyst.

Phase	Relative amount of Mo in phase
Mo(II) sulfide	47.2
Mo(IV) oxide	28.5
Mo(VI) oxide	24.3

Figure 4: Mo3d spectrum of aged catalyst.

A similar increase in oxidation is detected in the molybdenum spectra, shown in Figures 3 and 4.

As with the cobalt spectra, more oxidation was observed after exposure to air, leading to an increase in the relative amounts of Mo(IV) oxide and of Mo(VI) oxide at the surface and a decrease in the relative amount of Mo(II) sulfide.
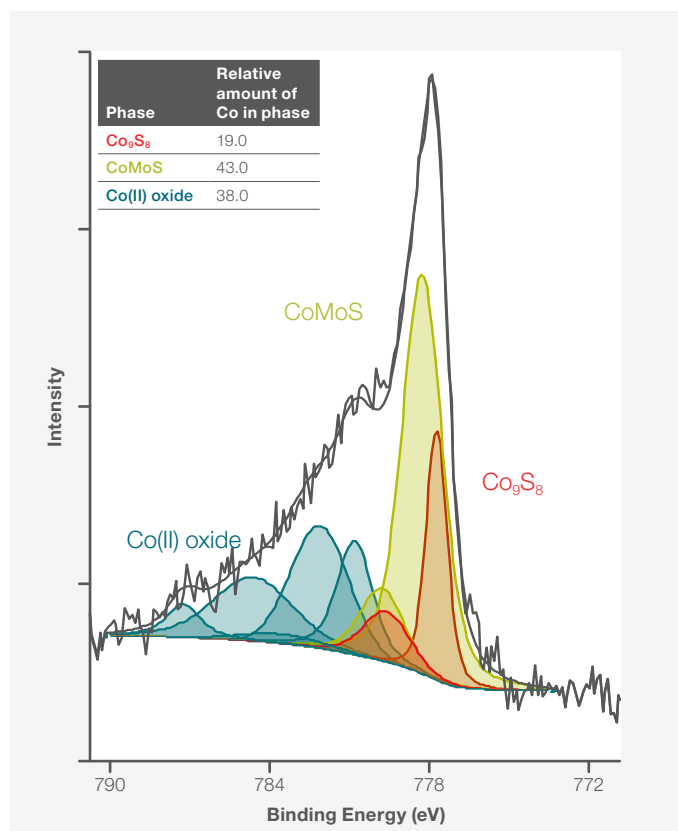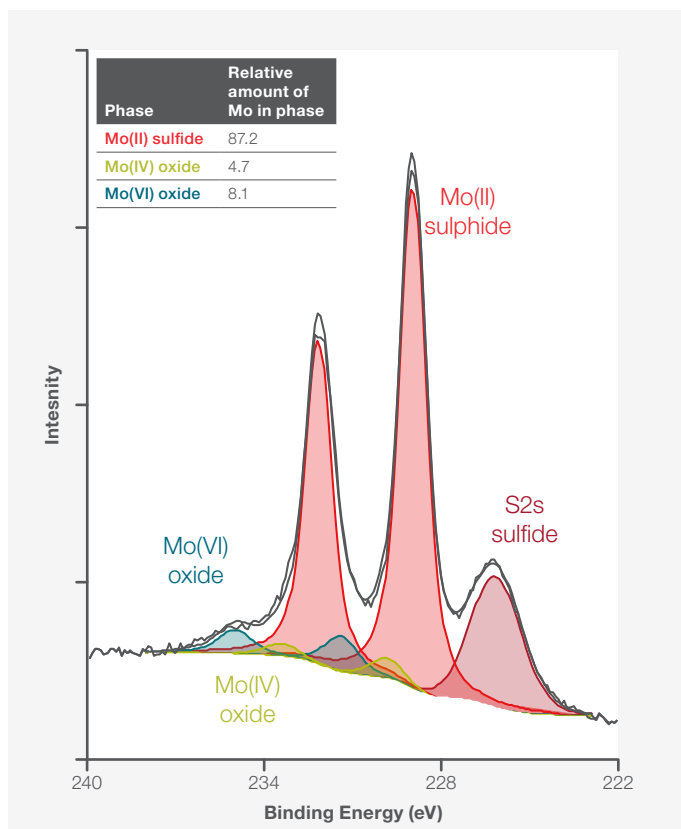
Table 1 shows the comparison table of the full chemical state quantification for the fresh and aged samples.

The quantification shows that the amount of alumina support has stayed the same and that the sulphur, molybdenum and cobalt have all become more oxidized. The identification of increased levels of oxidation enables the analyst to determine the quality of the surface of the catalyst.
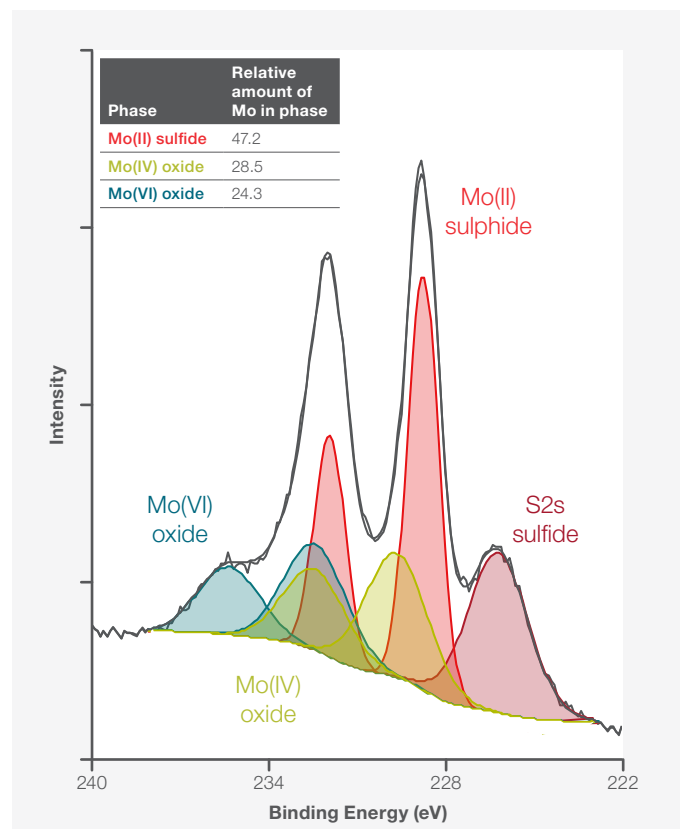
XPS peak	Chemical states	Fresh sample (Atomic percent)	Aged sample (Atomic percent)
Al2p	Al_2O_3	24.0	24.5
$S2p_{3/2}$	Sulfide	7.0	5.3
$S2p_{3/2}$	Oxysulfide	0.3	0.9
$Mo3d_{5/2}$	Mo (II) Sulfide	2.6	1.4
$Mo3d_{5/2}$	Mo (IV) oxide	0.1	0.9
$Mo3d_{5/2}$	Mo (VI) oxide	0.2	0.7
C1s	C-C / C-O / C=O	22.9	17.6
O1s	O-C / O-metal	40.8	46.1
Ni2p	Ni (II) sulfide	1.6	2.1
$Co2p_{3/2}$	Co_9S_8	0.1	0.1
$Co2p_{3/2}$	CoMoS	0.3	0.2
$Co2p_{3/2}$	Co (II) oxide	0.1	0.2

Table 1: Full chemical state quantification for both the fresh and aged sample.

Summary
The K-Alpha XPS System can be used to quickly and accurately identify and quantify the chemical states of the elements present in catalyst samples.

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References
1. Gandubert et al., Oil & Gas Science and Technology – Rev. IFP, Vol. 62 2007, No. 1, pp. 79-89

Keywords
K-Alpha, Cobalt Oxidation, Hydrodesulfurization Catalysis, Metal Oxides, Surface Analysis, XPS

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