APPLICATION NOTE

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Characterization of Molybdate type catalysts using benchtop ARL EQUINOX 100 XRD

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Introduction

Molybdates are well known as catalysts in selective oxidation of hydrocarbons. In terms of scale, the most common application is the usage as a precursor for catalysts in the hydrodesulfurization of refined petroleum products and natural gas. For the latter application, mostly RuS_2 is used but also Co-Mo containing compounds exhibit a very good activity. $NiMoO_4$ on the other hand is known to exhibit a very good selectivity in oxidation reactions of hydrocarbons. The catalytic activity of such materials strongly depends on the particle size and the ratio to the support material. For these types of materials, often Al_2O_3 is used as a support material, which often appear as a mixture of amorphous and crystalline fractions. The most commonly used method to determine both the crystallite size of nanoparticles and the quantitative composition of solid mixtures is X-ray diffraction (XRD). In XRD, the peak width of reflections is directly related to the size of the scattering domain through Scherrer's equation. Therefore, it is possible to determine the crystallite size (CS) by determining the width of reflection in the diffraction pattern. On the other hand, sophisticated whole pattern fitting (WPF, Rietveld method) approaches can quantify crystalline and amorphous contents with good accuracy in one joint refinement.

Instrument

The Thermo Scientific™ ARL™ EQUINOX 100 X-ray Diffractometer employs a custom-designed Co (15 W) micro-focus tube with mirror optics for high flux, which does not require external water chilling.

Figure 1: ARL EQUINOX 100 X-ray diffractometer

The ARL EQUINOX 100 XRD provides very fast data collection times thanks to its unique curved position sensitive detector (CPS) that measures all diffraction peaks simultaneously. It is therefore well suited for both reflection and transmission measurements (Figure 1).

Experimental

For XRD measurements, $NiMoO_4$ and $CoMoO_4$ powders were measured 45 min in reflection mode. Quantitative phase analysis and crystallite size determination (Scherrer's equation) was carried out using MDI JADE 2010 (WPF).

Results

Qualitative phase analysis reveals that both samples contain γ-Al_2O_3 and a significant amount of amorphous phase (most likely Al_2O_3). The Al_2O_3 acts as a support for the actual β-$CoMoO_4$ (Figure 2) and β-$NiMoO_4$ phases (Figure 3). Quantitative analysis (WPF) of all crystalline and amorphous phases reveal significant amounts of active Molybdate catalysts (c.f. Table 1) with crystallite size of 10 nm for both Molybdates.

Phase	Sample 1 (in wgt %)	Sample 2 (in wgt. %)
$CoMoO_4$	3.5	-
$NiMoO_4$	-	6.3
γ-Al_2O_3	59.0	61.6
Al_2O_3 (amorph.)	37.5	32.1

Table 1: Results from WPF quantification

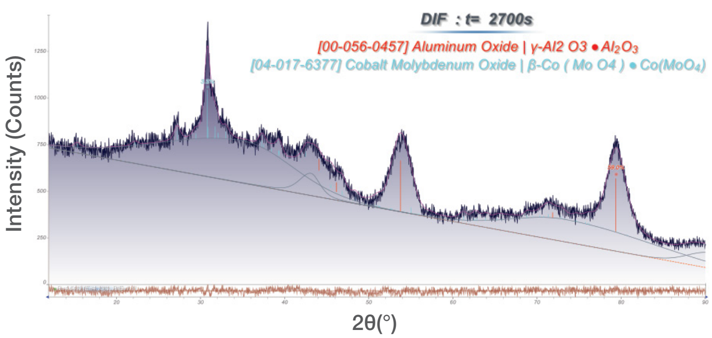

Figure 2: WPF of a $CoMoO_4$ sample

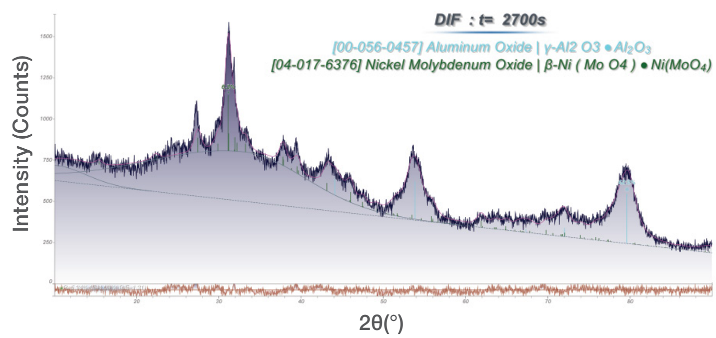

Figure 3: WPF of a $NiMoO_4$ sample

Conclusion

The benchtop ARL EQUINOX 100 XRD in combination with the MDI JADE 2010 software suite is a convenient solution to easily determine crystallite sizes and phase composition of Molybdate type catalysts. Refining both crystalline and amorphous phase in one joint refinement is a sophisticated and easy way to obtain all values relevant for characterizing the quality of such catalysts. The crystallite size of the active nanoparticles (10 nm) is in a typical range for such applications.

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