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Investigations of element spatial correlation in Mn-promoted Co-based Fischer–Tropsch synthesis catalysts ☆

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ABSTRACT

Making connections between performance and structure in bimetallic catalysts requires knowledge of how the two elements are spatially associated. Elemental maps obtained by analytical TEM methods are an invaluable tool for identifying the location of different elements, but for many samples, visual inspection of elemental maps is insufficient for assessing the degree of element spatial correlation. This is particularly true for beam-sensitive materials where short mapping acquisition times lead to images with high noise and low color depth. In these situations, statistical analysis of elemental maps can be used to identify spatial correlations among the elements in a sample. In this work, the relationship between catalyst performance and bimetallic spatial association was explored using Mn-promoted Co-based Fischer–Tropsch synthesis catalysts prepared by different pretreatment methods. Mn was used as a catalyst additive to suppress methane formation. Catalysts that underwent calcination before reduction produced more methane and fewer long-chain hydrocarbons than catalysts that were directly reduced. The extent to which Co and Mn were spatially associated was assessed using correlation metrics, colocation plots, and histograms generated using data from STEM–EDS maps. Although both catalysts yielded visually similar elemental maps, the results of statistical analysis suggested that the calcined catalyst exhibited greater spatial segregation between the Co and Mn. These findings support the hypothesis that having Mn in close proximity to the Co is essential for the manifestation of Mn promotion effects in Co-based FTS catalysts.

1. Introduction

Transmission electron microscopy (TEM) is a valuable tool for characterizing catalyst particles and has been widely applied in the field of heterogeneous catalysis to assess nanoparticle size and structure. This has been demonstrated for numerous systems containing Pt, Au, or other heavy transition metals [1–3]. However, for lighter transition metals such as Co and Cu, standard techniques such as bright-field TEM become more challenging due to the lower contrast of these elements against typical catalyst support materials such as silica, alumina, or titania. Scanning transmission electron microscopy with high-angle annular dark-field imaging (HAADF–STEM) produces images with contrast based on the atomic number of the material (Z-contrast), but this technique is of limited utility when investigating samples containing elements with similar atomic numbers, overlapping structures in projection, and uneven thickness [4]. For many catalyst systems, analytical electron microscopy methods such as energy dispersive spectroscopy (EDS) or electron energy-loss spectroscopy (EELS) are the only viable techniques for obtaining element-specific images with nanoscale resolution.

Acquiring elemental maps on particles or structures that are less than 10 nm in size means that the measured signal will be small. Particularly in EDS mapping, where X-ray generation by core-electron relaxation after excitation with the incident beam

☆ *Dedication:* This paper is dedicated in memory of Dr. Haldor Tøpsoe, the founder of Haldor Tøpsoe A/S and a leader in the development of new catalytic technologies. Throughout his career, Dr. Tøpsoe affirmed that an understanding of catalyst composition and structure was essential for the development of superior catalysts. The technique that particularly interested him was transmission electron microscopy because it enabled direct visualization of catalyst nanoparticles and the changes that they experience upon being used to promote chemical reactions. It is, therefore, appropriate that this article, which describes advanced TEM methods developed to provide a quantitative measure of the association of promoting elements with the element that are responsible for catalyst activity, is included in this special volume.

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is a low probability event, it is necessary to use more beam current than is typical for imaging or to use increased acquisition times for signal averaging [5]. However, small particles are often beam-sensitive, and the integrity of the map necessitates that the incident electrons do not impart enough energy to rearrange the material being mapped. The challenge then is to balance sample damage (requiring lower beam current or total dose) and spatial resolution with the collection of enough X-ray counts to make quantitative conclusions (requiring higher beam current or total dose). Even with proper optimization of map acquisition parameters, additional challenges exist pertaining to the interpretation of map data and the determination of how associated or segregated multiple elements are with respect to each other.

Often, the assessment of element spatial association relies upon visual inspection to identify structures of different compositions in the elemental maps [6–8]. However, this approach is insufficient when interpretable motifs do not exist or when the length scale of composition heterogeneity is similar to that of the map resolution. Moreover, comparisons among samples are difficult to make if the degree of element segregation varies throughout different regions of an individual sample. Statistical tools for analyzing image similarity represent a useful alternative approach, and there are abundant examples of these tools being applied toward microscopy research. Microbiologists have long made use of various correlation coefficients to quantify colocation of fluorescently labeled proteins within cells [9]. Using elemental maps obtained by energy-filtered TEM, Grogger et al. were able to infer the existence of various chemical phases in alloys and ceramics through multivariate histograms [10,11]. More recently, Parish and Brewer explored the application of principle component analysis toward STEM–EDS maps to count and identify distinct phases in ceramics [12]. Still, there has not been much evaluation of how statistical methods can be used to evaluate element segregation in samples for which sensitivity to beam damage is a prevailing concern.

These considerations about data interpretation are frequently present when studying industrially relevant catalysts, which often consist of a catalytically active metal and one or more catalytically inactive elements, referred to as promoters that serve to increase the activity, selectivity, or stability of the active element [13]. For example, Co metal is known to be an active catalyst for Fischer–Tropsch synthesis (FTS) of hydrocarbons from CO and H_2, and transition metal oxide promoters are frequently employed to improve product selectivity [14]. While several studies have shown that the addition of Mn limits the undesired formation of methane and enhances the formation of long-chain hydrocarbons used in diesel fuel, the means by which Mn affects the catalytic properties of Co are not well understood [15,16]. Boffa et al. and Sachtler et al. have hypothesized that adsorbed CO can interact simultaneously with Co metal sites and nearby Mn cations so as to weaken the carbonyl bond and facilitate CO dissociation [17,18]. If such a scheme were true, then it would imply that Mn oxide must be in contact with Co metal nanoparticles. Testing such a hypothesis requires analytical electron microscopy in order to understand the degree of spatial association between Co and Mn within these catalysts. Morales et al. have used STEM–EELS imaging to show that Mn locates preferentially close to Co in TiO_2-supported Co–Mn catalysts; however, these conclusions came from visual inspection of a small number of nanoparticles [19]. There are, therefore, compelling reasons for developing ways to avoid the risks of basing conclusions on non-representative images and subjective interpretations. There are compelling motivations for developing ways to avoid the risks of basing conclusions on non-representative images and subjective interpretations. In this work, we adapt existing methods and introduce new approaches for statistically evaluating the colocation of two elements from a set of EDS maps. We demonstrate that these methods can be used even when the total number of X-ray counts per pixel is low and where binning pixels would sacrifice too much spatial resolution. These methods are then used to analyze a Mn-promoted Co catalyst to show how changes in the pretreatment of this catalyst affect the spatial relationship of Mn and Co, which correlates with changes in catalyst product selectivity.

2. Experimental

2.1. TEM sample preparation

Catalyst precursors were prepared by impregnating porous silica (PQ Corporation, CS-2129) with an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$ (Sigma-Aldrich, 99.999% purity) followed by drying at room temperature overnight. The dried catalyst precursors were then calcined in flowing air (Praxair, zero grade) at 673 K or reduced in flowing H_2 (Praxair, 99.999% purity) at 673 K for 2 h with 4 K/min temperature ramps followed by passivation with 500 ppm O_2 in He (Praxair, 99.999% purity) at room temperature for 30 min. In this work, catalysts prepared by these two pretreatment methods are referred to as initially calcined and directly reduced catalysts, respectively. Co weight loading was kept constant at 10 wt% Co in all samples; Mn loading was varied to yield samples with Mn/Co atomic ratios of 0, 0.1, and 0.5. The bulk elemental compositions of all catalyst samples were verified by ICP–OES (Galbraith Laboratories).

TEM samples of the catalysts were prepared by grinding 5 mg of catalyst in a mortar for 30 s. The ground catalyst particles were then suspended in 1 ml of anhydrous hexane and ultrasonicated for 1 min. From this suspension, 5 μl was drop-cast onto an ultrathin carbon film with lacey carbon support Cu TEM grid (Ted Pella). To remove solvent, the sample grid was dried in a vacuum oven at 373 K at less than 0.1 bar for 1 h.

2.2. TEM and STEM imaging

Bright-field TEM images of the Co–Mn catalysts were acquired to assess particle size statistics using an FEI Tecnai T12 microscope at the Electron Microscopy Lab at UC Berkeley operated with an accelerating voltage of 120 kV. For each catalyst sample, approximately 300 nanoparticles were used to generate particle size distributions. The surface mean diameters, also known as the Sauter mean diameters, of the nanoparticles were calculated according to Eq. (1), where n_i is the number of particles with diameter d_i in a nanoparticle sample of size N [20]:

$$\bar{d} = \frac{\sum_i^N n_i d_i^3}{\sum_i^N n_i d_i^2} \tag{1}$$

More detailed imaging of the metal nanoparticles within the Co–Mn catalysts was done in STEM mode using an FEI Tecnai T20 microscope and an aberration-corrected FEI Titan 80-300 (TEAM I) at the Molecular Foundry at the Lawrence Berkeley National Laboratory. On both microscopes, images were collected using an accelerating voltage of 80 kV.

2.3. STEM–EDS mapping

Hyperspectral elemental maps were recorded using a FEI Titan electron microscope equipped with a 4 segment silicon drift detector with a 0.7 steradian solid angle at the Molecular Foundry at the Lawrence Berkeley National Laboratory. Images were acquired in scanning transmission electron microscopy (STEM) mode with a probe convergence semi-angle (α) of 10 mrad. High-angle annular dark-field (HAADF) images were acquired with inner semi-angles (β) greater than 70 mrad. The X-ray spectrum at each pixel was recorded from 0 to 10 keV with an energy resolution of 140 eV