Is There a Relationship Between the M=O Bond Strength of Bulk Mixed Metal Oxides and Catalytic Activity?

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Introduction

Over the years, the catalysis literature is replete with publications attributing the catalytic activity of bulk metal oxides to the strength of metal-oxygen double bond (M=O). Tarama et al. [1] studied the role of the V=O bond in bulk V_2O_5-based catalysts for oxidation reactions over bulk mixed V_2O_5-MoO_3 oxide catalysts and attributed the reactivity of the catalyst to the V=O bond. Trifiro et al. concluded that the dehydrogenating power of metal oxide catalysts such as bulk V_2O_5, MoO_3 and mixed metal molybdates is related to the strength of the M=O bond [2]. Furthermore, the Mars-van Krevelen mechanism was also cited in order to emphasize that the V=O bond is the catalytic active site for oxidation reactions by vanadium pentoxide-based catalysts [3]. These early qualitative publications have introduced the concept that the M=O bond of bulk metal oxides controls the catalytic activity into the catalysis literature and have been widely cited and embraced over the years.

In order to quantitatively examine this hypothesis, the surface reactivity of bulk mixed metal vanadate and molybdate catalysts were examined with CH_3OH-temperature programmed surface reaction (TPSR) spectroscopy and the M=O bond strengths were determined from Raman spectroscopy. The CH_3OH-TPSR experiment provides the first-order surface kinetic rate constant for breaking of the C-H bond of surface CH_3OH* and CH_3O* intermediates for the formation of HCHO [4]. Unlike the broad IR M=O bands that were previously examined in connection with the above studies, Raman spectroscopy gives rise to sharp M=O bands that reflect the M=O bond strength [5, 6]. The present study rigorously compares, *for the first time*, the relationship between the normalized specific surface reactivity for CH_3OH oxidation to formaldehyde and M=O bond strengths of bulk mixed metal vanadates and molybdates.

Catalyst Preparation and CH₃OH-TPSR Experiment

Detailed information about preparation methods and thermal treatment procedures for the bulk metal vanadates and molybdates can be found elsewhere [7, 8]. The experimental procedure followed for the CH_3OH-TPSR as well as the mathematical expression used for kinetic parameter estimation has been previously discussed [9]. In the present study the k_{rds}, the first-order rate constant for C-H bond breakage, for bulk vanadates and molybdates has been calculated at a T_{ref} (reference temperature) of 300 and 380 °C, respectively.

Results and Discussion

To rigorously examine the hypothesis that the bulk M=O bond strength controls the catalytic activity of bulk mixed metal vanadate and molybdate catalysts, the first-order k_{rds} rate constants are plotted for both catalytic systems as a function of bulk M=O bond Raman shift.

The M=O bond Raman shift is directly related to the M=O bond strength [5, 6], which means higher M=O Raman shift indicates stronger M=O bond strength. The M=O Raman shifts were obtained from the Raman spectra of the bulk mixed metal vanadates and molybdates and are plotted in Figure 1 vs. k_{rds}.
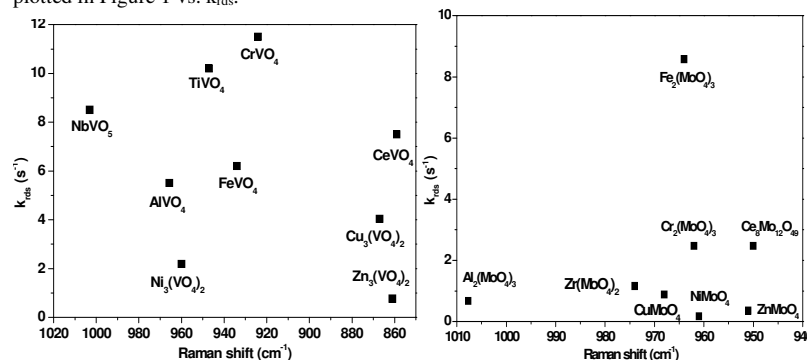

Figure 1. Relation between the k_{rds}, the first-order rate constant for formation of HCHO, and the Raman shift of the bulk M=O bond for (a) bulk mixed metal vanadates and (b) bulk mixed metal molybdates.

The absence of any correlation between the bulk M=O bond Raman shift and the intrinsic catalytic activity for CH_3OH oxidative dehydrogenation is not too surprising since the rate-determining-step in the CH_3OH oxidative dehydrogenation reaction is C-H bond breaking [4] and does not involve M=O bond breaking. Thus, the properties of the M=O bond strength or length should not affect the oxidative dehydrogenation reaction rate.

Significance

The present study quantitatively investigates, *for the first time*, a long held concept in catalysis by bulk mixed metal oxides between M=O bond strength and catalytic activity. Contrary to expectation, it is found that there is no relationship between the M=O bond strength and the specific reaction rate, k_{rds}, for CH_3OH oxidative dehydrogenation to HCHO over bulk mixed metal vanadate and molybdate catalysts.

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