CATALYTIC HYDROCARBON REACTIONS OVER SUPPORTED METAL OXIDES

Final Report

August 1, 1995 – July 31, 1999

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April 12, 2000

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY
UNDER GRANT NUMBER DE-FG03-95ER14570
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Overview

The research program focused on the catalysis of hydrodesulfurization (HDS) over molybdenum-based catalysts and how catalyst composition, redox ability, structure and neighboring sites control the catalytic properties of metal oxides. We sought to understand the catalytic features/sites that control hydrogenation, hydrogenolysis, and isomerization during HDS. Unpromoted silica-supported molybdenum oxides and molybdenum sulfides were studied. Model catalyst systems were prepared from organometallic precursors or cluster compounds to generate supported structures that feature Mo(II) and Mo(IV) cations that are isolated or in ensembles and that have either Mo-O or Mo-S bonds. Conventional MoS₂ catalysts, which contain both edge and rim sites, were be studied. Finally, single-layer MoS₂ structures were also prepared from 2H-MoS₂ powder so that the model systems could be compared against a disulfide catalyst that only involves rim sites. Catalytic reactions for thiophene and tetrahydrothiophene were studied over the various catalysts. Oxidation states were be determined using X-ray photoelectron spectroscopy. X-ray crystallography was used to characterize and follow changes in the MoS₂ structures. The program on metal oxides prepared supported oxides that have a specific structure and oxidation state to serve as model templates for the more complex commercial catalysts and then employed these structures in reaction studies. This focus area examined the relationships between structure and cation redox characteristics in oxidation catalysis. Infrared and Raman spectroscopy were used to characterize the cations and reaction intermediates.

The major finding are represented in the abstracts of the papers published from this work.

Degrees Granted under this Award

1998  David L. Sullivan (PhD)  Hydrodesulfurization of Thiophene, Tetrahydrothiophene and 1-Butanethiol on Model Silica-supported Molybdenum and Tungsten Catalysts
1998  Narayanan C. Ramani (PhD)  Reaction and Spectroscopic Study of Supported Metal Oxide Catalysts
1999  William P. Boone (MS)  Hydrodesulfurization Studies with Model Supported MoS₂ Catalysts
Publication Abstracts


Activity and product selectivity have been measured for thiophene hydrodesulfurization (HDS) over model silica-supported molybdenum catalysts at a pressure of 1 atm and at temperatures ranging from 398 to 673 K. The model catalysts feature isolated molybdenum atoms in the +2, +4, and +6 oxidation states and molybdenum dimers with each molybdenum atom in the +4 oxidation state. Silica-supported MoS₂, prepared by deposition and decomposition of (NH₄)₂MoS₄, was used for reference. There is a correlation between thiophene HDS activity and molybdenum oxidation state, with Mo(II) most active. Thiophene HDS activity does not show a significant structure dependence for isolated Mo(IV) versus dimeric Mo(IV) catalysts. Activation energies of 51.5 and 49.9 kJ/mol were determined for thiophene HDS over Mo(II) and MoS₂/SiO₂ catalysts, respectively. Butane and butenes are the major products of thiophene HDS with little butadiene detected. Activity and selectivity trends suggest the HDS reaction is initiated by η¹ binding of thiophene on the supported metal catalysts.


Isomerization of 1-butene on Mo(VI)/SiO₂, W(VI)/SiO₂, and Cr(VI)/SiO₂ was investigated by steady-state flow reactor studies and Fourier transform infrared spectroscopy. (η⁵-C₅H₅)₆M₂(CO)₆ or M(η¹-C₅H₅)₄ (M = Mo, W) were used as precursors in preparing Mo(VI)/SiO₂ and W(VI)/SiO₂ catalysts. Cr(NO₃)₃ was used to prepare Cr(VI)/SiO₂. Isomerization proceeds by a Brønsted catalyzed pathway involving alkoxide intermediates and an oxidative dehydrogenation pathway involving allylic intermediates. Flow reactor experiments revealed that two pathways for isomerization could be observed with Mo(VI)/SiO₂: through the alkoxide intermediate at T < 523 K and through the allylic intermediate at T > 573 K. W(VI)/SiO₂ catalysts were more active for isomerization than Mo(VI)/SiO₂ catalysts, but the demarcation of the two pathways was not as clear. Only the oxidative dehydrogenation pathway for isomerization was observed for the
Cr(VI)/SiO₂ catalysts at \( T > 473 \) K. In IR studies, alkoxide intermediates were observed following adsorption of 1-butene on Mo(VI)/SiO₂ and W(VI)/SiO₂ catalysts at 300 K; complete desorption of the surface alkoxide occurred by 532 K. The surface species observed for adsorption of 1-butene on Cr(VI)/SiO₂ at 300 K were typical of allylic C-H abstraction; these surface species transform into deep oxidation products on heating, resulting in a surface that is poisoned. Pyridine adsorption studies reveal traces of Brønsted acidity on Mo(VI)/SiO₂, W(VI)/SiO₂, and Cr(VI)/SiO₂. Brønsted acidity would account for the alkoxide mechanism of 1-butene isomerization. The reason that these Brønsted acid sites are most active for 1-butene isomerization on W(VI)/SiO₂ and inactive on Cr(VI)/SiO₂ is discussed.


Removal of organosulfur compounds from petroleum is accomplished by hydrodesulfurization (HDS) in which the petroleum is reacted with hydrogen on a supported metal sulfide catalyst. The typical catalyst consists of cobalt-promoted molybdenum disulfide supported on γ-alumina. The MoS₂ is present as small crystallites with cobalt atoms located on the perimeter of the crystallites. MoS₂ crystallites present three crystal faces. The basal plane (0001) is terminated by sulfur atoms that are bound to three molybdenum atoms. Sulfur vacancies (active sites) are not formed on the basal plane and it is inactive for HDS. The perimeter of the crystallites exhibits (10\( \bar{1} \)0) and (1010) crystal faces (2). The (1010) face is terminated by sulphydryl groups (-SH) in which the sulfur atoms are bound to only one molybdenum atom (terminal sulfur). The (10\( \bar{1} \)0) face is terminated by sulphydryl groups in which the sulfur atoms are bound to two molybdenum atoms (bridging sulfur). The active sites for HDS have been shown to be molybdenum atoms that are located on the crystal perimeter. These active molybdenum atoms are thought to have one or more sulfur vacancies and be in an oxidation state lower than the 4+ of molybdenum in the bulk of MoS₂. However, the details of the oxidation state and structure of the active sites are unknown. Spectroscopic and chemisorption studies suggest the presence of reduced molybdenum on CoMoS/Al₂O₃. The
complexity of the industrial catalyst has made definitive identification and quantification of reduced molybdenum difficult. Also, the presence of a large amount of Mo(IV) (bulk MoS₂) has made it difficult to correlate reduced molybdenum with HDS activities and selectivities. We have used isolated Mo(II), Mo(IV) and Mo(VI) to study oxidation state effects in HDS and have used isolated Mo(IV), dimeric Mo(IV) and MoS₂/SiO₂ to study structural effects in HDS.

**The Influence of Metal Oxide Additives on the Molecular Structures of Surface Tungsten Oxide Species on Alumina: I. Ambient Conditions (M. M. Ostromecki, L. J. Burcham, I. E. Wachs, N. Ramani, and J. G. Ekerdt) J. Molecular Catalysis A: Chemical 132, 43 (1998).**

The molecular structures of WO₃/Al₂O₃ catalysts, with and without the presence of secondary metal oxide additives (P, Sn, Fe, Ni, Zn, Ce, Co, La, Ca, Mg, K and Na), were determined with Raman spectroscopy under ambient conditions where the surface is hydrated. The hydrated surface tungsten oxide species found on the alumina support (WO₄²⁻, HW₆O₁₉⁻, and U-metatungstate) were related to the net pH at the point of zero charge (pzc) of the thin aqueous layers. The isolated tungstate species was dominant at high pH values and the polytungstate species were dominant at lower pH values. The net pH at pzc was a function of tungsten oxide loading (decreasing from 8.9 to 4.4 for 1 to 25% WO₃/Al₂O₃, respectively) and the specific secondary metal oxide additive (Na > K > Mg > Ca > La > Co > Ce > Zn > Ni > Fe > Sn > P). Below monolayer coverages, the secondary metal oxide additives preferentially interacted with the alumina support to form surface metal oxide species rather than with the tungsten oxide species to form mixed tungsten oxide crystalline compounds. Above monolayer coverages, both surface metal oxide species and mixed tungsten oxide crystalline compounds were formed. The more basic secondary metal oxide additives (Ca, La) formed mixed tungsten oxide crystalline compounds. In the absence of the formation of mixed tungsten oxide crystalline compounds, the alumina support was able to accommodate approximately two monolayer-equivalents of the surface metal oxides during calcination because the surface tungsten oxide species and the secondary surface metal oxide species occupied different sites on the alumina support. The surface tungsten oxide species preferentially interacted with the surface hydroxyls of the alumina.
support and the secondary surface metal oxide species preferentially interacted with coordinately unsaturated $\text{Al}^{3+}$ sites.


The role of surface structure and cation red-ox nature was investigated for the selective oxidation of 1-butene over SiO$_2$-supported Mo(VI), Cr(VI), and W(VI) oxide catalysts. X-ray diffraction and Raman spectroscopy were used to characterize the surface structures over the different catalysts. The surface structure of Mo(VI)/SiO$_2$ was controlled by using different preparation methods. An aqueous route using $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}^-$ led to a catalyst that had dispersed Mo along with small crystallites of MoO$_3$. Organometallic routes using $(\text{C}_5\text{H}_5)_2\text{Mo_2(CO)}_6$ and Mo$(\text{C}_3\text{H}_7)_3$ led to completely dispersed Mo(VI)/SiO$_2$. Cr(NO$_3$)$_3$ was used to prepare completely dispersed Cr(VI)/SiO$_2$. In the case of W(VI)/SiO$_2$, the dispersion depended on the type of SiO$_2$ employed. The activity to formation of 1,3-butadiene revealed a structure effect for the Mo(VI)/SiO$_2$ catalysts, with crystalline Mo(VI) having a higher activity than dispersed Mo(VI). The red-ox ability of the supported cation was seen to have a dominating effect for this reaction. The turnover number for the formation of 1,3-butadiene followed the order Cr(VI)/SiO$_2$ > Mo(VI)/SiO$_2$ >> W(VI)/SiO$_2$, which is in agreement with the red-ox ability Cr > Mo > W. The importance of red-ox ability is discussed in terms of the allylic abstraction mechanism that is involved in selective oxidation.


Hydrodesulfurization (HDS) activities and selectivities were measured for thiophene, tetrahydrothiophene (THT), and 1-butane thiol on silica-supported molybdenum catalysts at a pressure of 1 atm and temperatures ranging from 530 to 795 K. The model catalysts, which were previously characterized, feature isolated molybdenum atoms in the +2, +4, and +6 oxidation states and molybdenum dimers with each molybdenum atom in the +4 oxidation state. Silica-
supported MoS₂ was used for reference. Activities for thiophene and THT HDS correlate with oxidation state. Mo(II) is most active among dispersed catalysts. 1-Butanethiol activities were much larger than thiophene or THT activities and were roughly equal on all dispersed catalysts. Apparent activation energies of 43.4 and 48.5 kJ/mol were determined for thiophene HDS on Mo(II) and MoSₓ/SiO₂, respectively. Apparent activation energies of 132 and 174 kJ/mol were determined for THT HDS on Mo(II) and MoSₓ/SiO₂, respectively. Dihydrothiophene, THT and 1-butanol were formed in thiophene HDS over Mo(II) and MoSₓ/SiO₂. The major products of thiophene and THT HDS were 1-butene, 2-butene, and n-butene. Butadiene, i-butane, i-butene, methane, ethane, ethene, propane, and propene were formed in small amounts. Butadiene is thought to be the initial product of thiophene and THT desulfurization and undergoes subsequent hydrogenation and isomerization to yield the observed products. A common mechanism for HDS of thiophene and THT with 2,5-DHT as an intermediate is discussed.


Alumina-supported single-layer MoS₂ was prepared and its hydrodesulfurization (HDS) activity compared to an alumina-supported multilayer MoS₂ catalyst. Single-layer crystallites were formed by exfoliation of lithium-intercalated 2H-MoS₂ crystals and were deposited on γ-alumina at pH 10.5-11. The single-layer material is shown to be stable under reaction conditions and catalytic, with similar activity and selectivity relative to the multilayer catalyst in the HDS of thiophene and tetrahydrothiophene.