

Preparation and Characterization of a New Ternary Chromium(III)–Molybdenum(VI) Oxide $\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$

Roger Bühler,* John R. Günter,*¹ and Christian Baerlocher†

*Institute for Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland; and †Laboratory of Crystallography, ETH-Zentrum, CH-8092 Zürich, Switzerland

Received July 18, 1997; in revised form May 12, 1998; accepted May 22, 1998

A new mixed oxide was prepared by coprecipitation of $\text{Cr}(\text{NO}_3)_3$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ from aqueous solution and subsequent calcination. The ternary oxide with the general stoichiometry $\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$ was characterized by X-ray diffraction (XRD), thermoanalysis (TA), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), atomic absorption spectroscopy (AAS), and Raman scattering. The new oxide showed the typical temperature-dependent electric conductivity known for semiconductors. The structure was refined with the Rietveld method from powder diffraction data. It is strongly related to the hexagonal chromiumsesquioxide structure. Preliminary catalytic experiments revealed a low combustion rate for methane but an increasing preference for C–C coupling reactions with higher Mo content. © 1998 Academic Press

INTRODUCTION

Molybdenum containing ternary oxides have been intensively investigated for their catalytic, electric, and magnetic properties. This investigation was performed in order to find new ternary chromium–molybdenum oxides with different oxidation states of the metal ions. Both chromium and molybdenum are known to occur in oxidation states between –II and +VI.

The most commonly known phases in the Cr–Mo–oxide system are $\text{Cr}_2(\text{MoO}_4)_3$ (2, 3), CrMoO_4 (4), and Cr_2MoO_6 (5) (the latter being only available by high-pressure synthesis).

The systems $(\text{Cr}, \text{Mo})\text{O}_2$ (6, 7) and especially $(\text{Cr}, \text{Mo})_2\text{O}_3$ (8) have not been extensively described. Our work focused on the synthesis, characterization, and catalytic behavior of the ternary oxide $\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$.

¹To whom correspondence should be addressed.

EXPERIMENTAL SECTION

Preparation of $\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$ with $x = 0.155$ (8.4 at.% Mo)

Sixteen grams of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka Puriss p.a.) were dissolved in 200 ml of distilled water and poured together with a solution of 649 mg $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Fluka puriss p.a.) in 60 ml of distilled water. The mixture was stirred and heated in a beaker until 3/4 of the water had evaporated. The highly viscous solution was placed into a furnace and slowly heated from 40° to 160°C for more than 12 h to dryness. The resulting dark green powder was ground in a ball mill, pressed to a pellet, and calcined in a furnace in air for 12 h at 560°C and another two hours at 680°C. This procedure resulted in a black powder exhibiting a diffraction pattern similar to that of Cr_2O_3 . The crystallinity depended only on the low temperature step. A very slow drying process gave larger crystallites. Several samples were prepared with a Mo content ($[\text{Mo}]/([\text{Mo}] + [\text{Cr}])$) ranging from 4.9 to 8.4 at.%. Higher Mo contents resulted in an impurity phase identified as $\text{Cr}_2\text{Mo}_3\text{O}_{12}$.

CHARACTERIZATION METHODS

XRD

The powder diffraction patterns were measured with a Philips diffractometer X'Pert using a graphite monochromator and $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with silicon as internal standard.

AAS

The disintegration of the mixed oxide was achieved by oxidative melting in $\text{KHCO}_3/\text{KNO}_3$ (1:1) and subsequent dissolution in an aqueous HNO_3 solution. Pure Cr_2O_3 and MoO_3 were used to determine the regain rate. Measurements were performed on an AAS spectrometer 2100 (Perkin–Elmer, Norwalk, CT).

EDX

EDX measurements were carried out with pressed pellets of the powder on a scanning electron microscope SEM 515 (Philips, Eindhoven/NL) equipped with an X-ray detector EDX 5400 (Tracor Northern, Middleton). The quantification of the spectra was done using CrK- and MoL-lines with ZAF-correction.

TA

Thermogravimetric analyses in air were carried out in Al_2O_3 crucibles which were heated in a furnace up to 1400°C for 2 h. MoO_3 started sublimating at $\sim 600^\circ\text{C}$, while Cr_2O_3 remained as pure phase. The weight loss was measured with a precision balance (Mettler Instrumente AG, Greifensee/CH). Measurements under hydrogen (flow rate 30 ml/min, heating rate $10^\circ/\text{min}$) were made on a thermal analyzer TA 2000C (Mettler Instrumente AG, Greifensee/CH).

XPS

XPS spectra were collected with $\text{MgK}\alpha$ radiation on an XPS spectrometer Kratos S800-XPS (Kratos Analytical, Manchester, UK) using pressed pellets. The binding energies indicated that both chromium and molybdenum ions were octahedrally coordinated. Chromium existed in the oxidation state III (Cr $2p^{3/2}$: 577.2 eV (9)) while molybdenum occurred in its highest oxidation state VI (Mo $3d^{5/2}$: 232.7 eV (10)).

Raman Scattering

These experiments were made by means of a Labram II Raman microscope (DILOR Instruments SA) with laser excitation (He-Ne laser, 632.816 nm) at the Paul Scherrer Institute (PSI), Villigen.

RESULTS

The three chromium–molybdenum–oxides S1, S2, S3 were prepared and characterized by the above-described methods (see Table 1).

Thermoanalytical semi-quantitative analysis was based on the observation that in thermoanalysis under hydrogen Mo(VI) was fully reduced to metallic molybdenum at temperatures above 600°C . The reduction of Mo(VI) was very slow and occurred in one step, whereas chromium remained in the oxidation state III. The sluggish reduction was completed only at 1100°C . Sublimation of MoO_3 was not observed in reductive H_2 -atmosphere. Pure MoO_3 , in

TABLE 1
Mo Content $[\text{Mo}]/([\text{Cr}]+[\text{Mo}])$ Determined by Various Measurements

$\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$ (theor.)	S1	S2	S3
$[\text{Mo}]/([\text{Cr}] + [\text{Mo}])$ (theor.)	5.0%	6.5%	8.4%
EDX	4.7%	6.6%	8.5%
AAS	5.2%	6.5%	8.5%
TA	4.7%	6.6%	8.0%
average	4.9%	6.6%	8.4%
σ	0.25%	0.06%	0.24%

contrast, is reduced in a fast two-step reduction (via MoO_2) between 550° and 780°C under identical conditions.

Raman scattering clearly confirmed that no residual MoO_3 had remained in the samples, as the spectrum was distinctly different from that of MoO_3 and the characteristic peaks of this compound were missing, but it was very similar to that of Cr_2O_3 .

The synthesized $\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$ was nano-crystalline (< 10 – 80 nm, according to scanning electron micrographs). Thermal treatment in air did not result in a better crystallinity but led to a phase segregation (Cr_2O_3 , MoO_3) at temperatures above 600°C . It had no effect at lower temperatures. Qualitative electronic measurements using pressed pellets revealed that the ternary oxide was a far better semiconductor than the pure chromiumsesquioxide and that its electrical conductivity depended strongly on the temperature. The energy bandgap estimated from the variation of the conductivity with temperature was about 0.5 eV.

Preliminary catalytic experiments carried out with a mixture of oxygen and methane in helium revealed a low combustion rate. $T_{50\%}$ was $> 600^\circ\text{C}$, though much higher than $T_{50\%}$ for the pure chromiumsesquioxide. A low combustion rate for methane and an increasing preference for C–C coupling with higher Mo content were observed. Details are omitted here, as no surface area measurements have been made.

RIETVELD REFINEMENT

The diffraction pattern of the new ternary oxide was very similar to that of Cr_2O_3 (chromiumsesquioxide). However, significant differences were evident with respect to the integrated intensities and the full width at half maximum (FWHM) of the peaks. The peaks were very broad, ranging from 0.25° to $60^\circ 2\theta$ and the pattern showed strong anisotropic line broadening. Unfortunately, a simple rule for the hkl dependence of the FWHM could not be discerned.

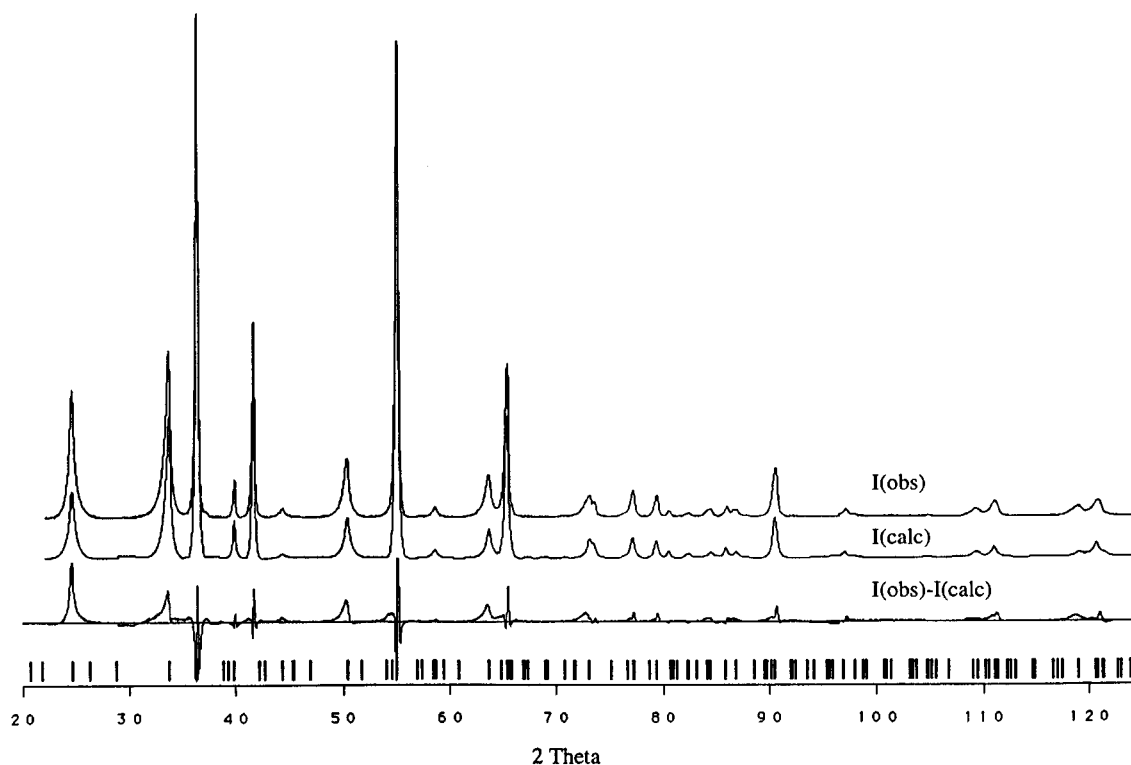


FIG. 1. Rietveld refinement of sample S2 (6.6 at.% Mo).

The Rietveld refinement was performed on a diffraction pattern of sample S2 with the program XRS-82 (11), which allowed individual values for the FWHM of the peaks to be set. For most reflections, the FWHM could be measured by hand, but for some reflections it had to be estimated. These measurements were used as initial values and then refined in groups of similar FWHM. The coordinates of chromium sesquioxide (1) were used as a starting model and a difference Fourier map was calculated. This revealed a strong peak in 0,0,0, the corresponding position of which was partially filled with Mo(VI). The refinement progressed only to the following R values: $R_{wp} = 0.37$, $R_B = 0.20$. As can be seen from the Rietveld plot (Fig. 1), the differences are partly due to incorrect modeling of the peak shapes, but, to a large extent, they are the result of individual peak shifts, which could not be modeled with the program. The reasons for the strong line broadening and line shifts are distortion and stress phenomena in the crystallites. Considering that these phenomena were not included in the structural model, the resulting agreement between observed and calculated intensities is acceptable. Nonetheless, the resulting parameters should not be over interpreted.

The Mo-content was refined to 6 at.%, which is in reasonable agreement with the expected value of 6.6 at.% (see Table 2).

STRUCTURAL ASPECTS

The structure of $\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$ (Fig. 2) is strongly related to the hexagonal structure of chromiumsesquioxide (Cr_2O_3) (1) and the hexagonal close packed oxygen arrangement remains unaffected. Two neighboring chromium(III) ions are substituted by one molybdenum(VI) ion, which is placed on the equivalent crystallographic (0,0,0) or (0,0,1/2) sites lying on the lattice plane-type $\{1-11\}$. As there are 12 chromium ions per unit cell, 2 chromium ions replaced by one molybdenum ion would result in a stoichiometry of

TABLE 2
Refined Atomic Parameters of Sample S2 (6.6 at.% Mo)

Atom	x	y	z	U	PP
Cr	0	0	0.3455(4)	2.01(1)	0.888(8)
Mo	0	0	0	1.9(1)	0.112(4)
O	0.315(3)	0	0.2500	1.4(1)	

Note. Lattice constants (hexagonal): $a = 4.944(2)$, Ref. (1), (Cr_2O_3) $a = 4.9607(10)$; $c = 13.569(6)$, Ref. (1), (Cr_2O_3) $c = 13.599(5)$.

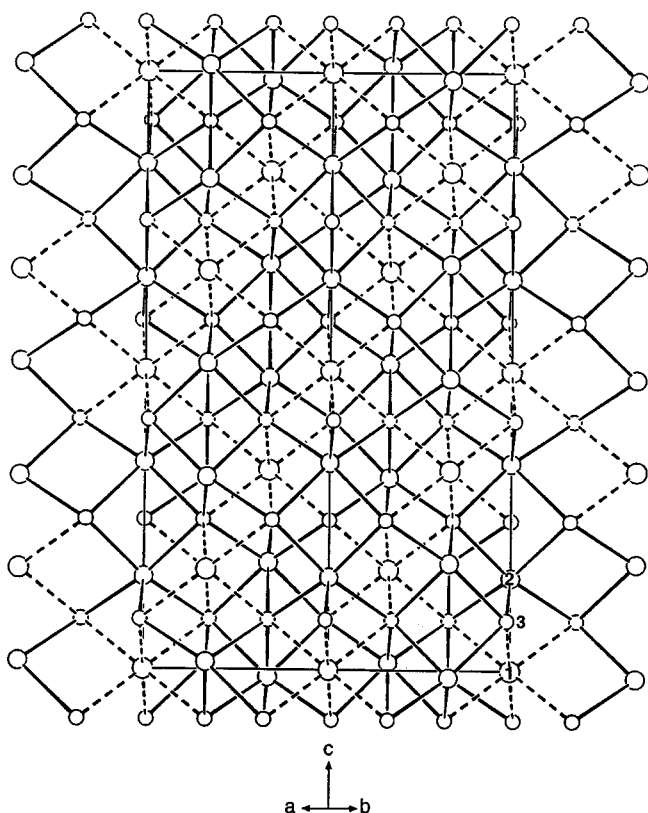


FIG. 2. Unit cell of $\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$ viewed along the $[110]$ direction: (1) Mo-site, octahedral coordination plotted with dashed lines, (2) O-site, and (3) Cr-site, octahedral coordination plotted with solid lines.

$\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$ with $x = 1/6$. Therefore, the synthesized mixed oxides with a smaller x -value must be considered as solid solutions, molybdenum being statistically placed on the special sites mentioned above. The structure is illustrated by Fig. 3.

CONCLUSIONS

$\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$ is a new metastable compound with a structure based on that of, and lattice constants similar to those of, Cr_2O_3 , each Mo replacing two neighboring Cr ions. This mixed oxide, synthesized from aqueous solution, is nanocrystalline and thus has a large surface area. No sintering was observed after thermal treatment at 580°C for one week in air, the crystallite size was not affected at all. As a matter of fact, the ternary oxide is not accessible through the simple mixture of chromium and molybdenum oxides or metals, followed by heating. These solid state reactions only result in the thermodynamically stable phases $\text{Cr}_2\text{Mo}_3\text{O}_{12}$, CrMoO_4 , and the binary oxides of Cr and Mo.

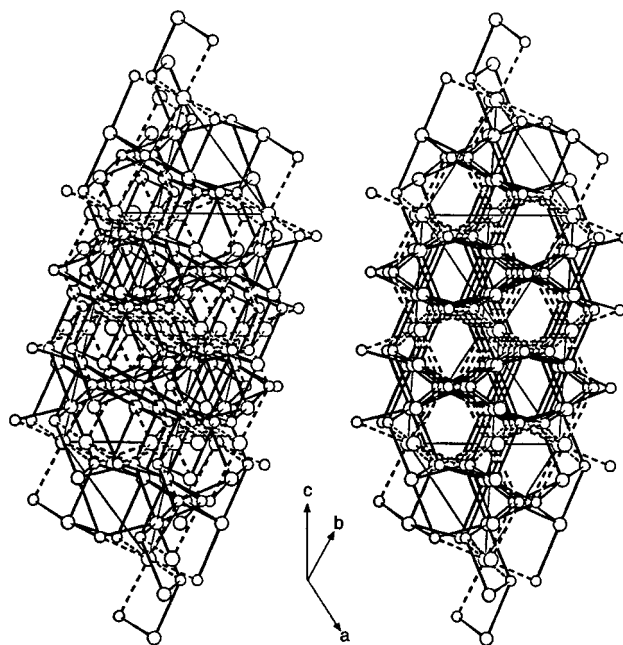


FIG. 3. Stereo view of $\text{Cr}_{2-2x}\text{Mo}_x\text{O}_3$ along the $[1-11]$ direction.

ACKNOWLEDGMENTS

Thanks are due to Ralph Eichenberger for the AAS measurements, Armin Portmann for EDX and SEM analyses, and J.-C. Panitz (PSI, Villigen) for the Raman data.

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