*Bulletin of the Chemists and Technologists of Macedonia*, Vol. **24**, No. 2, pp. 153–155 (2005)
GHTMDD – 473 ISSN 0350 – 0136
Received: March 25, 2005 UDC: 54–31.057
Accepted: November 25, 2005

*Short communication*

# A NOVEL METHOD FOR SYNTHESIS OF $Cr_2O_3$, $MnO_2$, $MoO_3$ AND $WO_3$

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$Cr_2O_3$, $MnO_2$, $MoO_3$ and $WO_3$ oxides were synthesized by a new reaction of urea with ($K_2CrO_4$ or $K_2Cr_2O_7$), $KMnO_4$, $Na_2MoO_4$ and $Na_2WO_4$, respectively, in an aqueous media at ~ 85 °C. Infrared spectra, X-ray powder diffraction, and microanalysis of the solid products, indicate the absence of urea, and the presence of oxides. A general mechanism describing the formation of oxides and decomposition of urea is suggested.

**Key words:** $Cr_2O_3$; $MnO_2$; $MoO_3$; $WO_3$; urea

## INTRODUCTION

Urea is known to be the parent compound of a large and interesting class in both organic and inorganic compounds; it is used as a starting material for the synthesis of many applied compounds. The literature reveals that urea is forming coordinate bonds with many metal ions at room temperature in aqueous and non aqueous media through its oxygen or nitrogen atoms, depending on the type of metal ion used [1–8]. From a chemical viewpoint, the reaction of metal salts with urea at high temperature has recently gained increasing interest [7–14]. The nature of the reaction products depends strongly on the type of metal ions and the metal salts used. Our previous studies [7–14] concerning the reaction of urea with metals such as Co(III), Pb(II), Sn(II), Cr(III), Fe(III), Au(III), Sn(IV), V(V) and Mo(IV) at high temperature demonstrate that the types of metal ions, beside their anions, have a pronounced effect on the nature of the reaction products. This led to discovering a novel method for preparation $PbCO_3$ and $CoCO_3$ [10], lanthanide carbonates [12], limonite, FeO(OH) [9], $2ZnCO_3{\cdot}3Zn(OH)_2$ [8], and $SnOCl_2{\cdot}2H_2O$ [7]. The aim of this publication is to report the synthesis and characterization of the $Cr_2O_3$, $MnO_2$, $MoO_3$ and $WO_3$ oxides resulting from a novel oxidation reduction reaction between ($K_2CrO_4$ or $K_2Cr_2O_7$), $KMnO_4$, $Na_2MoO_4$ and $Na_2WO_4$, respectively, with urea, in an aqueous solution at ~ 85 °C.

## EXPERIMENTAL

All chemicals used through out this study were Analar or extra pure grade. The leaf green oxide, $Cr_2O_3$, was prepared by mixing equal volumes of aqueous solutions of 0.1M of $K_2CrO_4$ or $K_2Cr_2O_7$ and 0.6M of urea. The mixture was heated on a water bath to approximately 85°C for about ~12 h. The precipitate was filtered off, washed several times with bidistilled water, and dried in vacuo over $CaCl_2$. The three oxides, $MnO_2$ (black), $MoO_3$ (gray white) and $WO_3$ (canary yellow) were prepared in a manner similar to that described above by the reaction of $KMnO_4$, $Na_2MoO_4$ and $Na_2WO_4$, respectively, with urea. The elemental analysis for the obtained products shows the absence of carbon, hydrogen and nitrogen elements. The percentage of chromium, molybdenum and tungsten were determined by using an atomic absorption method. A spectrometer model PYE-UNICAM SP 1900 fitted with the corresponding lamp was used for this purpose. The

infrared spectra of the reactants and the solid products obtained were recorded from KBr discs using a Gensis II FT IR Spectrophotometer. The X-ray diffraction patterns for the $MoO_3$ under investigation was recorded on Philips X-ray powder diffraction 1390, fitted with an ionization detector. CuKα radiation was used at 35 KV and 25 mA, at the National Research Center, Cairo, Egypt.

## RESULTS AND DISCUSSION

The reaction of aqueous solutions of urea with potassium (chromate and dichromate), permanganate and sodium (molybdate and tungestate) produces leaf green colored oxide, $Cr_2O_3$; black solid oxide, $MnO_2$; gray white oxide, $MoO_3$, and canary yellow oxide, $WO_3$. The formation of these oxides upon the heating of an aqueous mixture of $K^+$ and $Na^+$ salts with urea may be described as follows:

$$1 - 2K_2CrO_4 + 2CH_4N_2O \xrightarrow{85\ ^oC} 2K_2CO_3 + Cr_2O_3 + 2NH_3 + N_2 + H_2O$$

$$2 - K_2Cr_2O_7 + CH_4N_2O \xrightarrow{85\ ^oC} K_2CO_3 + Cr_2O_3 + NH_3 + NO_2 + 1/2H_2$$

$$3 - 2KMnO_4 + CH_4N_2O \xrightarrow{85\ ^oC} K_2CO_3 + 2MnO_2 + NH_3 + NO_2 + 1/2H_2$$

$$4 - Na_2MoO_4 + CH_4N_2O + 1.5O_2 \xrightarrow{85\ ^oC} Na_2CO_3 + MoO_3 + N_2 + 2H_2O$$

$$5 - Na_2WO_4 + CH_4N_2O + 1.5O_2 \xrightarrow{85\ ^oC} Na_2CO_3 + WO_3 + N_2 + 2H_2O$$

For the first three reactions, a reduction process for Cr(VI) and Mn(VII) to Cr(III) and Mn(IV) occurs during the decomposition of urea into ammonia and carbon dioxide. The infrared spectra of urea and the oxides products are shown in Figure 1. There are no bands due to the characteristic groups of urea (carbonyl and amide groups), but the bands associated to the oxides are observed [15]. Confirming these results are the data obtained from elemental analysis, determination of metals (Cr(III), Mn(IV), Mo(VI) and W(IV)), and the fact that infrared spectra of commercially obtained $Cr_2O_3$, $MnO_2$, $MoO_3$ and $WO_3$ are the same as that of the reaction products. Furthermore, the X-Rray diffraction pattern of the product resulting from the reaction between $Na_2MoO_4$ and urea at elevated temperature (Fig. 2) is matched by that of commercially available $MoO_3$ [16].

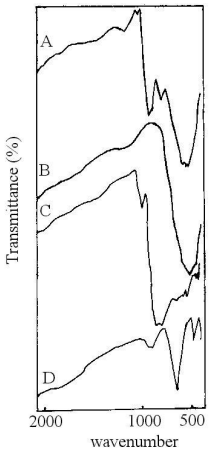


**Fig. 1.** Infrared spectra of the product resulting from the reaction of urea with ($K_2CrO_4$ or $K_2Cr_2O_7$), $KMnO_4$, $Na_2MoO_4$ and $Na_2WO_4$, respectively.
(A): $Cr_2O_3$, (B): $MnO_2$, (C): $MoO_3$, (D): $WO_3$

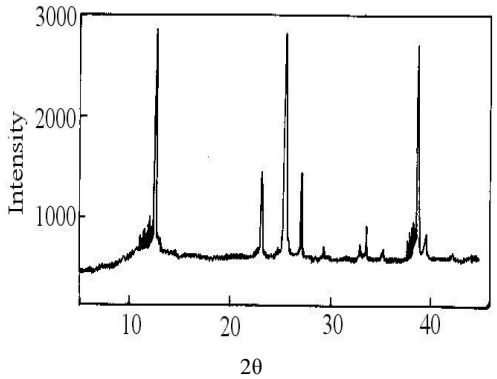


**Fig. 2.** X-ray powder diffraction of the product resulting from the reaction of urea with $Na_2MoO_4$

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Р е з и м е

## НОВА ПОСТАПКА ЗА СИНТЕЗА НА $Cr_2O_3$, $MnO_2$, $MoO_3$ И $WO_3$


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**Клучни зборови:** $Cr_2O_3$; $MnO_2$; $MoO_3$; $WO_3$; уреа


Со примена на нова реакција на уреа ($K_2CrO_4$ или $K_2Cr_2O_7$), $KMnO_4$, $Na_2MoO_4$ и $Na_2WO_4$, поединечно во водни раствори на температура од 85 °C, е извршено синтетизирање на оксидите $Cr_2O_3$, $MnO_2$, $MoO_3$ и $WO_3$. Инфрацрвените спектри, прашкастата дифракција со Х-зраци и микроанализите на цврстите продукти покажаа отсуство на уреа, а присуство на оксиди. Прикажан е генерален механизам што ги опишува декомпозицијата на уреата и формирањето на оксидите.