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Alkali Phosphomolybdates for Oxidation of Methacrolein to Methacrylic Acid

The purpose of this paper is to report the characterization of a number of alkali phosphomolybdate catalysts used for studies on the oxidation of methacrolein. These very active catalysts were discovered by White and Rege (*1*) for the vapor-phase oxidation of acrolein and methacrolein to acrylic and methacrylic acid, respectively.

Experimental. The molybdate catalysts were formed in the general-type system R_2O–P_2O_5–MoO_3 where R is sodium, potassium, rubidium, cesium, or ammonium ions. The catalysts were formed by mixing solutions of ammonium molybdate, diammonium hydrogen phosphate, and alkali chlorides. The solutions were heated to 90°C while stirred continuously until precipitates formed and then were evaporated to dryness. Small amounts of titanium and vanadium promoter ions were incorporated by adding solutions of either titanium oxalate or ammonium vanadate during the coprecipitation step. The catalysts were dried at 95°C overnight and then calcined at 450°C in air for 16 hr. The crystalline phases in the catalyst were determined by X-ray diffraction using a Picker diffractometer and CuK_α radiation. Thermogravimetric analysis was used to determine decomposition temperatures for pure alkali phosphomolybdates. Promoted and unpromoted catalysts were also examined by infrared absorption using a Beckman 12 spectrophotometer. The calcined catalysts were pressed into wafers and placed in the infrared cell, evacuated at 25°C for 1 hr, and then exposed to methacrolein (25°C, 70 mm pressure).

Catalytic activity for the partial oxidation of methacrolein to methacrylic acid was evaluated in a stainless-steel fixed-bed reactor equipped with a full-length thermowell. Ten milliliters of catalyst was charged in the reactor and heated in a flow of air to reaction temperature. After a brief steam treatment, the feed was introduced and the reaction stream was adjusted to a methacrolein/oxygen/steam/nitrogen molar ratio of 1/1.5/7.2/12. The contact time was 2 sec based on total gas throughput at 350°C. Liquid products were condensed at −78°C and were analyzed in water solution by gas chromatography using a flame detector. The off-gas was metered and analyzed by gas chromatography. Formaldehyde, acetic acid, and carbon oxides were the principle by-products. The data in Table 1 were calculated for 67 ± 5 mmole carbon through the reactor each hour.

Crystals of potassium phosphomolybdate tetrahydrate [$K_3PO_4(MoO_3)_{12} \cdot 4H_2O$] and ammonium phosphomolybdate [$(NH_4)_3PO_4(MoO_3)_{12} \cdot 4H_2O$] were prepared using the precipitation method determined by the National Bureau of Standards (*2*). The color of the potassium phosphomolybdate is greenish yellow while that of the ammonium phosphomolybdate is a deep yellow. Lattice constants of these pure crystals were determined by mounting a thin film of powder on the diffractometer. The instrument was set at a takeoff angle of 2.5°; a 0.002 receiving slit and a 1/8°/min scanning speed were used. Fourteen intensity maxima were measured for 2θ between the values of 26° and 87° with silicon powder used as both an

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TABLE 1

Catalyst Activity Data for Partial Oxidation of Methacrolein to Methacrylic Acid

Catalyst	Temperature[a] (°C)	Percentage conversion	Percentage selectivity	Yield (methacrylic acid)
Mo_6PO_x	425	35	56	20
Mo_9PO_x	425	35	52	18
$Mo_{12}PO_x$	425	32	53	17
Mo_9PRbO_x	350	73	64	47
$Mo_9PRb_{1.5}O_x$	350	67	62	42
$Mo_9PRbV_{.15}O_x$	375	60	70	42
$Mo_9PRb_{1.5}V_{.15}O_x$	375	85	65	55
$Mo_9PRb_{1.5}Ti_{.15}V_{.15}O_x$	375	75	67	50
$Mo_9PRbTi_{.15}O_x$	375	66	66	44
$Mo_9PRbTi_{.30}O_x$	350	80	55	44
Mo_9PKO_x	425	11	21	2
Mo_9PCsO_x	375	68	66	45

[a] Temperature is for hottest part of catalyst bed.

internal and external standard. Similar conditions were used for the catalyst samples except Cu$K\alpha_{\text{mean}}$ was used because the α_1, α_2 doublet could not be resolved. Eight measurements of center of gravity for 2θ between the values 26° and 63° were made. Additional measurement of peak widths at half-height for the (222) reflection of the phosphomolybdates and the silicon (111) reflection from a single silicon crystal were also made for estimating crystallite size.

Discussion. The catalytic activity of the molybdenum phosphates and the unpromoted and promoted alkali phosphomolybdate catalysts are given in Table 1. The molybdenum phosphate catalysts give much lower yields of methacrylic acid than those catalysts containing rubidium ions. The addition of small amounts of titanium and vanadium ions gives a small improvement in the selectivity. Results for potassium- and cesium-promoted phosphomolybdates are also given.

The X-ray diffraction analyses of the catalysts show that the principal crystalline phase in the molybdenum phosphates is molybdenum oxide. The addition of rubidium results in the formation of the species $Rb_3PO_4(MoO_3)_{12}$ that coexists with molybdenum oxide. These phases persist with the addition of vanadium and titanium promoter ions. The unit cell lengths of the rubidium phosphomolybdate in the catalyst along with the pure isostructural hydrated analogs containing potassium and ammonium ions are given in Table 2. The unit cell length of the rubidium phosphomolybdate is slightly larger than that of either the potassium or ammonium phosphomolybdates. The crystallite sizes of the potassium

TABLE 2

Lattice Parameters and Crystallite Sizes of Alkali Phosphomolybdates

	$K_3PO_4(MoO_3)_{12} \cdot 4H_2O$	$(NH_4)_3PO_4(MoO_3)_{12} \cdot 4H_2O$	$Rb_3PO_4(MoO_3)_{12}$
a (Å)	11.5959(*8*)	11.6685(*6*)	11.6741(*16*)
Crystal size (Å)	1550	1450	800

and ammonium forms are nearly equivalent and are about twice the size of the rubidium phosphomolybdate. This is probably due to the formation of the hydrated potassium and ammonium forms by precipitation from solution as compared to the formation of the rubidium phosphomolybdate at elevated temperature during calcination. Furthermore the dehydration of these phosphomolybdates does not result in a collapse of the structure. The rehydration characteristics were not examined.

Thermogravimetric analyses of the potassium and ammonium phosphomolybdates showed that our potassium form lost 1.4 wt% with the substantial weight loss occurring at about 100°C. This is less than the 3.58 wt% loss expected for the fully hydrated crystals. This may be due to some loss occurring during drying of the precipitated crystals at 90°C. Fusion of the potassium form to a glass occurred at about 700°C. The weight loss curve for the ammonium phosphomolybdate is given in Fig. 1. The four water molecules are lost at about 100°C. Further weight loss is observed starting at about 400°C from the loss of ammonium ions in the structure resulting in the evolution of ammonia and water. The weight losses for the ammonium form agree well with the weight losses expected for the four water molecules and three ammonium ions per molecular formula for the structure.

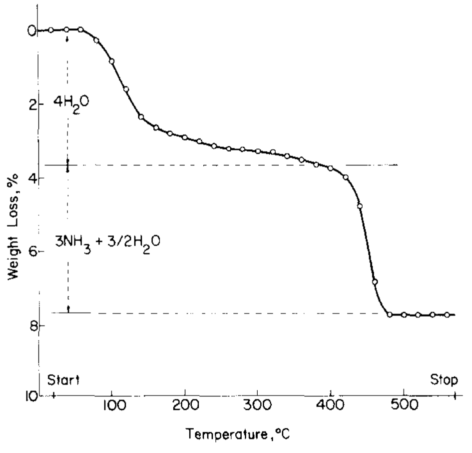

FIG. 1. Thermogravimetric analysis of ammonium phosphomolybdate.

FIG. 2. Infrared patterns for molybdenum phosphate (before and after methacrolein exposure (a) and rubidium phosphomolybdate; before (b) and after (c) methacrolein exposure.

The infrared data for the molybdenum phosphate and the rubidium phosphomolybdate catalysts before and after exposure to methacrolein are given in Fig. 2. The infrared data show that methacrolein is chemisorbed on the rubidium phosphomolybdate surface as evidenced by absorption frequencies at 1380, 1460, and 1730 cm^{-1} which correspond to frequencies observed for gaseous methacrolein. Methacrolein adsorption on the unpromoted surface was not observed which may be responsible for the lower activity of the unpromoted molybdenum phosphate.

Conclusion. The addition of rubidium to molybdenum phosphate catalysts gives a much more active catalyst for the oxidation of methacrolein to methacrylic acid. This increased activity is correlated with the formation of $Rb_3PO_4(MoO_3)_{12}$ which coexists with molybdenum oxide. The rubidium phosphomolybdate structure present in the catalyst is similar to that of the hydrated potassium and ammonium phosphomolybdates. Titanium- and vanadium-promoted rubidium phosphomolybdate catalysts offer a slight improvement over the unpromoted catalysts.

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