



SUPPLEMENTARY MATERIAL TO
**(N(But)₄)₅H₄PV₆Mo₆O₄₀ as an efficient catalyst for the oxidative
desulphurisation of gasoline**

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PREPARATION OF THE V-CONTAINING CATALYSTS

Preparation of H₄PMo₁₁VO₄₀

A stoichiometric mixture of 0.49 g of phosphoric acid, 0.45 g of vanadium pentoxide and 7.2 g of molybdenum trioxide was suspended in 150 mL of distilled water. The mixture was stirred for 6 h at 80 °C. After cooling down to room temperature and removal of the insoluble molybdates and vanadates, the heteropolyacid solution was evaporated and dried at 85 °C for 24 h, whereby orange crystals of H₄PMo₁₁VO₄₀ were obtained.¹

Preparation of (N(But)₄)₄H[PMo₁₀V₂O₄₀]

Sodium metavanadate (12.2 g, 100 mmol) was dissolved by boiling in 50 mL of water and then mixed with 3.55 g (25.0 mmol) of Na₂HPO₄ in 50 mL of water. After the solution had cooled, concentrated sulphuric acid (5 mL, 85 mmol) was added, whereby the solution developed a red colour. Then, Na₂MoO₄·2H₂O (60.5 g, 250 mmol) dissolved in 100 mL of water was added to the red solution under vigorous stirring, followed by the slow addition of a solution of 1.0 g (3.7 mmol) of tetrabutylammonium bromide in 5.0 mL of H₂O. The mixture was stirred at 60 °C for 3 h. The formed white precipitate of the desired product was filtered off, recrystallized from acetonitrile and diethyl ether, and air dried.¹

Preparation of (NH₄)₅H₄PV₆Mo₆O₄₀

To a solution of NaVO₃ (3.66g, 30 mmol) in water (19 mL) was added Na₂MoO₄·2 H₂O (4.11g, 17 mmol) in water (6 mL). To the resulting solution, 85 % H₃PO₄ (3.8 g, 30 mmol) in water (5 mL) was added dropwise, and the mixture was stirred for 1 h at 95 °C. After cooling the reaction mixture to 0 °C, a sufficient amount of aqueous saturated ammonium chloride solution was added to the solution to give a brown precipitate. The resulting precipitate was recrystallized twice from water to form clean brown crystals of (NH₄)₅H₄PV₆Mo₆O₄₀.²

Preparation of (N(But)₄)₅H₄PV₆Mo₆O₄₀

In the same manner, to K₁₀[P₂W₁₈Cd₄O₆₈] in 55 mL of warm distilled water was added a solution of 1.0 g (3.7 mmol) of tetrabutyl ammonium bromide in 5.0 mL of H₂O to give

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(NH₄)₅H₄PV₆Mo₆O₄₀. After cooling the reaction mixture to 0 °C, a solution of 1.0 g (3.7 mmol) of tetrabutylammonium bromide in 5.0 mL of H₂O was added slowly. The mixture was stirred at 60 °C for 3 h. The formed white precipitate was filtered off, recrystallized from acetonitrile and diethyl ether, and air dried.

DISCUSSION OF THE ASTM D-4294 STANDARD METHOD

In the ASTM D-4294 standard test method for analysis of the samples, a cup was filled to about 75 % of its capacity with the sample to be measured. Before filling the cell, it may be necessary to heat viscous samples so that they are easy to pour into the cell. Ensure that no air bubbles are present between the cup window and the liquid sample. Measure each sample once. If the concentration from the first analysis is less than 100 mg kg⁻¹, the measurement is repeated using a freshly prepared sample cup and a fresh portion of the sample, and the average of the readings for the sulphur content in the sample is obtained.

This test method covers the determination of total sulphur in petroleum and petroleum products that are single-phase and either liquid at ambient conditions, liquefiable with moderate heat, or soluble in hydrocarbon solvents. These materials can include diesel fuel, jet fuel, kerosene, other distillate oil, and naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasohol, biodiesel and similar petroleum products.

In the case of petroleum materials that contain suspended water, it is recommended that the water be removed before testing or that the sample be thoroughly homogenized and immediately tested. The interference is greatest if the water creates a layer over the transparent film as it will attenuate the X-ray intensity for sulphur. One such method to accomplish the removal of water is to centrifuge the sample first under ambient sealed conditions, taking care that the sample integrity is not compromised.

Summary of this test method. The sample is placed in the beam emitted from an X-ray tube. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration samples to obtain the sulphur concentration in mass % and/or mg kg⁻¹. A minimum of three groups of calibration samples are required to span the concentration range: 0.0 to 0.1 mass %, 0.1 to 1.0 mass % and 1.0 to 5.0 mass % of sulphur. This test method provides rapid and precise measurement of the total sulphur in petroleum and petroleum products with a minimum of sample preparation. A typical analysis time is 1 to 5 min per sample.

REFERENCES

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