Immobilized Ionic Liquids Based on Molybdenumand Tungsten-Containing Heteropoly Acids: Structure and Catalytic Properties in Thiophene Oxidation

I. G. Tarkhanova^{*a*}, *, A. V. Anisimov^{*a*}, A. K. Buryak^{*b*}, A. A. Bryzhin^{*a*}, ^{*c*}, A. G. Ali-Zade^{*a*}, A. V. Akopyan^{*a*}, and V. M. Zelikman^{*a*}

^aFaculty of Chemistry, Moscow State University, Moscow, Russia ^bFrumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia ^cMendeleev University of Chemical Technology, Moscow, Russia *e-mail: itar_msu@mail.ru Received January 18, 2017

Abstract—Comparative analysis of heterogeneous catalysts for the peroxide oxidation of thiophene is conducted. The catalysts are imidazole ionic liquids (ILs) containing anions of phosphomolybdic and phosphotungstic acids immobilized on mineral supports. Immobilization is implemented by the covalent bonding of an IL fragment to a silica surface or by adsorption on alumina. The catalysts are active not only in the model oxidation of thiophene in isooctane, but also in the desulfurization of a straight-run diesel fraction and the "synthetic crude oil" derived from oil shale.

Keywords: thiophene oxidation, hydrogen peroxide, immobilized metal-containing ionic liquids, phosphomolybdic and phosphotungstic heteropoly acids

DOI: 10.1134/S0965544117100164

In recent years, the use of catalyst composites synthesized by the immobilization of ionic liquids (ILs) on porous materials with a developed surface has become increasingly common [1]. Synthetic approaches consist in the formation of ultrathin IL layers containing a transition-metal derivative, typically, in the anionic form. Immobilization is implemented by the covalent bonding of an IL fragment to a silica surface or by adsorption. These methods make it possible to significantly decrease the IL consumption and simplify the procedure for separating the reaction products from the catalyst.

IL-based heterogeneous catalysts are used in a variety of processes; a promising direction is the use of immobilized ILs—most often imidazole—for the oxidative desulfurization of petroleum feedstocks [2–8]. Analysis of the literature suggests that the most active composites include derivatives of Mo- and W-containing Keggin-type heteropoly acids (HPAs), in particular, phosphomolybdates and phosphotungstates.

The aim of this study is the synthesis and comparative analysis of heterogeneous catalysts based on the above compounds supported on silica and alumina by different methods. The model substrate is thiophene, which is the most difficult-to-oxidize compound in the series of sulfur-containing derivatives contained in petroleum feedstocks [9]. The catalysts are tested, in addition to a thiophene solution, in the desulfurization of a straight-run diesel fraction and "synthetic crude oil" derived from oil shale.

EXPERIMENTAL

Catalyst Synthesis by the Covalent Immobilization of an IL (I, Scheme 1)

The preparation of silicas modified with an imidazole IL was described in detail in [8, 10]. The dehydroxylation of the surface of a BASF Perlkat 97-0 silica gel (specific surface area, $S_{sp} = 500 \text{ m}^2/\text{g}$; effective pore diameter, $d_{eff} = 10 \text{ nm}$) was implemented by azeotropic distillation. To this end, the silica gel and toluene placed in a 100-mL round-bottomed flask equipped with a Dean-Stark head and a reflux condenser were boiled until the cessation of water evolution. After that, 3-chloropropyltrimethoxysilane was added to the mixture in the flask in a ratio of 1:4 with respect to silica gel and boiled under stirring for 6 h. Next, the solid phase was decanted, washed with toluene, and air-dried. Quaternization was implemented as follows: the support modified with 3-chloropropyltrimethoxysilane was placed in a glass tube and impregnated with ethylimidazole (four- to fivefold excess); the tube was evacuated to a residual pressure (10^{-2} torr) , sealed, and subjected to thermal conditioning at 180°C for 24 h. After that, the sample was removed from the tube, washed with rectified ethanol from excess ethylimidazole, and air-dried to constant weight.

Phosphomolybdic (PMA) and phosphotungstic (PTA) HPAs were deposited via the exchange reaction (Scheme 1). To this end, 0.5 g of PMA (or 0.6 g of PTA) was dissolved in ethanol (15 mL); the solution

was admixed with a weighed portion (1 g) of Perlkat modified by the above method; the resulting mixture was stirred for 24 h. The liquid phase was decanted; the solid residue was washed twice with alcohol and subjected to a procedure described in [11]. Light-end products were removed from the sample placed in a tube in a vacuum at $85-90^{\circ}$ C. This method was used to synthesize PMo-SiO₂ and PW-SiO₂ catalysts.



Scheme 1. Deposition of HPAs on a modified silica gel; m = 2-5; n = 7-13; l = 2-7; and k = 4-20.

Catalyst Synthesis by Adsorption (II, Schemes 2, 3)

Two milliliters of ethylimidazole and 3 mL of dichloroethane were placed in a glass tube; the tube was evacuated to 10^{-2} Torr under cooling with liquid

nitrogen, unsealed, and subjected to thermal conditioning at 100°C for 7 h. The resulting gray-brown salt crystals were washed twice with ethyl acetate (10 mL) and air-dried.



Scheme 2. Synthesis of 1-chloroethyl-3-ethylimidazolium chloride.

A metal-containing IL (Scheme 3) was synthesized by a modified procedure described in [12]. One gram of the molten IL—1-chloroethyl-3-ethylimidazolium chloride—was added dropwise to an aqueous solution of PMA (3 g per 10 mL of ice water) cooled to 0° C. After that, the aqueous phase was decanted, and the solid residue was air-dried.



Scheme 3. Synthesis of 1-chloroethyl-3-ethylimidazolium phosphomolybdate and 1-chloroethyl-3-ethylimidazolium phosphotungstate.

In the case of PTA, 2.3 g of molten 1-chloroethyl-3-ethylimidazolium chloride was added dropwise to an aqueous solution of PTA (2.6 g in 10 mL of water) under stirring at room temperature. After that, the aqueous phase was decanted, and the solid residue was air-dried.

The immobilization of 1-chloroethyl-3-ethylimidazolium phosphomolybdate and 1-chloroethyl-3ethylimidazolium phosphotungstate on γ -Al₂O₃ ($S_{sp} = 180 \text{ m}^2/\text{g}$; pore diameter, $d_{eff} = 1 \text{ nm}$) was conducted at room temperature. One gram of 1-chloroethyl-3ethylimidazolium phosphoromolybdate was dissolved in 15 mL of ethyl alcohol; the solution was admixed with a weighed portion of γ -Al₂O₃ (4 g); the resulting mixture was held in a Branson-1200 ultrasonic bath for 15 min. The resulting solution was decanted; the solid phase—a PMo/Al₂O₃ sample—was air-dried.

1-Chloroethyl-3-ethylimidazolium phosphorotungstate (1.8 g) was dissolved in 15 mL of ethyl alcohol; the solution was admixed with a weighed portion of γ -Al₂O₃ (7.2 g); the resulting mixture was stirred on a magnetic stirrer for 12 h. The aqueous phase was decanted; the solid PW/Al₂O₃ sample was air-dried.

Catalyst Composition and Structure Determination Procedures

The content of molybdenum and tungsten on the catalyst surface was determined photometrically using catechol, which forms a stable complex compound with molybdate and tungstate in the presence of sodium sulfite and sodium hydroxide [13, 14]. The analyzed catalyst sample was heated in concentrated sulfuric acid (1 mL) at 100°C for 3 h. After cooling, the resulting solution was transferred to a graduated cylinder and diluted to 10 mL with distilled water. After that, it was neutralized with an aqueous NaOH solution to a pH of 6. The catechol solution was prepared as follows: 1.5 g of sodium sulfite was added to 50 mL of a 0.4% sodium hydroxide solution in a graduated cylinder. After salt dissolution, 1 g of catechol was added under stirring; the solution volume was adjusted to 100 mL with distilled water.

To provide the photometric determination of molybdenum, 2 mL of a molybdic acid solution and 10 mL of a catechol solution prepared as described above were mixed; the optical density of the resulting mixture at 420 nm was measured. The amount of tungsten was determined by a similar procedure, while measuring the optical density at 350 nm. Electronic spectra were recorded on an Ocean Optics HR4000CG-UV-NIK instrument.

Data on the molecular composition of the compounds and their distribution over the catalyst surface were derived by surface-assisted laser desorption/ionization (SALDI) mass spectrometry. Mass spectra for the test samples were recorded in the RN Pep Mix mode on a Bruker Ultraflex instrument equipped with a nitrogen laser (wavelength, 337 nm; energy, 110 μ J) using a time-of-flight mass analyzer. The spectra were recorded in the negative ion detection mode using a reflectron. Cluster ions were identified with respect to isotopic distribution using the IsoPro simulation software [15].

The acidic properties of the catalysts were studied by temperature-programmed desorption of ammonia (NH₃ TPD) on a Unisit USGA-101 sorbent analyzer. The sample was calcined in a dry helium stream at 150°C and then cooled to room temperature. Adsorption of ammonia (diluted with nitrogen in a ratio of 1 : 1) was conducted at 60°C for 30 min. The physically sorbed ammonia was purged in a helium stream at 100°C for 1 h. NH₃ TPD experiments were conducted in a temperature range of 60–600°C in a dry helium stream (feed rate of 30 mL/min). The heating rate was 8°C/min.

Catalytic Testing and Product Analysis Procedures

The catalytic activity of the immobilized ILs was measured for the following three model processes.

Thiophene oxidation with hydrogen peroxide in isooctane. Ten milliliters of a model mixture (1 wt %, 0.076 M thiophene solution in isooctane), 0.08 g of the catalyst, and an oxidizer-35 or 50% hydrogen peroxide in different amounts (0.4-0.8 mL)—were placed in a thermostated reactor. The mixture in the reactor was stirred under heating (50 -70° C), while taking samples for analysis from the liquid phase when required.

Organic compounds in the reaction mixture were identified by nuclear magnetic resonance (NMR). Spectra were recorded on a Bruker Avance 600 instrument at room temperature. The products contained in the aqueous phase were analyzed by electrospray ionization (ESI) mass spectrometry. High-resolution spectra were recorded on a Bruker micrOTOF II instrument. The mass range was 50-3000 m/z. Measurements were conducted at the Department of Structural Studies, Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences.

Quantitative analysis of the liquid phase in the reaction mixture was conducted by gas-liquid chromatography (GLC) using a Kristall 4000 chromatograph equipped with a 2-m-long packed column with the SE-30 stationary phase (nonpolar silicon) and a flame-ionization detector. The content of thiophene and thiophene oxidation products was determined by the internal standard method with linear temperature programming of 90–220°C.

Oxidative desulfurization of a $180-360^{\circ}C$ straightrun diesel fraction produced at the Ryazan refinery. Ten milliliters of the fuel (total sulfur of 8800 ppm), 53–111 mg of the catalyst, and 1.13 mL of an oxidizer (35% hydrogen peroxide) were added to a jacketed reactor equipped with a magnetic stirrer. The mixture was stirred at a temperature of 60°C for 3 h. After that, to remove the oil oxidation products and the catalyst residues, the mixture was sequentially washed with water, twice with a 95% dimethylformamide solution in water, and again with water (in all cases, a volume ratio of 1 : 1).

| No. | Catalyst | Synthesis method | Metal content in catalyst, wt % | Maximum thiophene conversion, % |
|-----|------------------------------------|------------------|---------------------------------|------------------------------------|
| 1 | PMo-SiO ₂ | Covalent honding | 4.5 | 45 |
| 2 | PW–SiO ₂ | Covalent bonding | 12 | 51 |
| 3 | PMo/Al ₂ O ₃ | Adsorption | 2 | 53 |
| 4 | PW/Al ₂ O ₃ | Ausorption | 6 | 66 |

Table 1. Catalyst sample composition, synthesis method, and catalytic properties in the model reaction (10 mL of a thiophene solution in isooctane, 0.08 g of the catalyst, 0.4 mL of 35% H₂O₂)

Oxidative desulfurization of synthetic crude oil derived by oil shale extraction (Slantsy-2 settlement, Leningrad oblast) in straight-run gasoline ($40-160^{\circ}$ C fraction). The extraction pyrolysis of oil shale is described in detail in [16]. Ten milliliters of the feed-stock (total sulfur content of 1375 ppm), 5–17 mg of the catalyst, and 0.2 mL of an oxidizer (35% hydrogen peroxide) were placed in a thermostated reactor. The mixture was stirred at 60°C for 3 h. The product was purified as described for the second model process. Analysis of the fuel was conducted by X-ray fluorescence method on a Spectroscan Max (M-049-S/98) X-ray fluorescence spectrometer.

RESULTS AND DISCUSSION

Catalyst Composition and Physicochemical Characteristics

Spectrophotometric analysis data on the determination of the content of Mo and W on the surface of the synthesized catalysts are shown in Table 1.

According to the data, the metal concentration on the catalyst surface depends on the synthesis method and the nature of the support; the use of method I provides an increase in the metal content. This finding is apparently attributed to the fact that the specific surface area of the silica gel is larger than that of Al_2O_3 .

The use of the different supports and synthesis methods also affects the structure of ions on the surface, as evidenced by SALDI mass spectrometry data shown below. Figures 1a and 2a show the mass spectra of feed PMA and PTA.

These data suggest that the peaks in the mass spectra of PMA (Fig. 1a) correspond to the $PMo_{11}O_{35}^-$, $PMo_9O_{33}^-$, $PMo_8O_{30}^-$, $PMo_5O_{18}^-$, and $PMo_4O_{16}^-$ ions. The mass spectra of PTA (Fig. 2a) exhibit peaks of the $PW_{12}O_{40}^-$, $PW_7O_{20}^-$, $PW_6O_{17}^-$, $PW_5O_{15}^-$, $PW_4O_{14}^-$, $PW_3O_{12}^-$, $PW_2O_5^-$, and PWO_6^- ions.

The mass spectra of the catalysts synthesized by method I are shown in Figs. 1b and 2b.

Comparison of the spectra in Figs. 1a and 1b shows that, in the case of molybdenum derivatives, the formation of catalysts on the SiO₂ surface leads to the HPA degradation and the formation of polymolybdates, which are evident in the mass spectra as the following negative ions: $Mo_2O_7^-$, $Mo_4O_{12}^-$, and Mo_5O_{13} [8]. At the same time, the structure of the W-containing catalyst comprises the metal in the form of HPA anions, as evidenced by comparison of the spectra in Figs. 2a and 2b. The cluster compositions of feed PTA and the imidazole derivative of this HPA on the silica gel are close: the mass spectrum of the latter exhibits phosphotungstate ion peaks containing up to 12 metal ions.

HPA anions are more stable on the modified Al_2O_3 surface. The presence of HPA in the PMo/Al₂O₃ and PW/Al_2O_3 catalysts is confirmed by the occurrence of peaks of ions corresponding to large clusters in the mass spectra: $Mo_6O_{21}^-$, $PMo_5O_{18}^-$, $PMo_4O_{15}^-$, and $PMo_3O_{1\overline{2}}$ (Fig. 1c) and $PW_8O_{\overline{28}}$, $PW_{10}O_{\overline{34}}$, and $PW_{12}O_{40}^{-}$ (Fig. 2c). However, comparative analysis of the spectra of pure PMA and the PMo/Al₂O₃ sample shows that the formation of the latter leads to the partial degradation of large particles: the cluster ions contain no more than 6 Mo atoms, while the mass spectra of pure PMA exhibit ion clusters with 12 Mo atoms. In the case of formation of an IL based on PTA (PW/Al₂O₃ sample), the anions do not undergo degradation: the spectrum exhibits peaks of large ion clusters containing 10-12 W atoms. These results are consistent with the literature data on a higher stability of PTA compared with that of PMA and the degradation of HPA anions during the deposition of PTA on a γ -Al₂O₃ surface [17, 18].

Thus, analysis of the mass spectra of the catalysts synthesized by the different methods suggests that imidazole derivatives of HPAs can be immobilized on a γ -Al₂O₃ surface without any cardinal degradation of anions. This finding is apparently attributed to the specific features of synthesis by the adsorption method: in this case, the stage of formation of a metal-

PETROLEUM CHEMISTRY Vol. 57 No. 10 2017



Fig. 1. SALDI mass spectra of (a) PMA, (b) the PMo $-SiO_2$, and (c) PMo $/Al_2O_3$ catalysts recorded in the negative ion detection mode.

containing IL precedes the deposition of the IL onto the surface. In the procedure involving a silica gel, the catalyst is formed owing to the reaction between the HPA and the IL already immobilized on the support; in this case, the anions of PMA and PTA undergo complete and partial degradation, respectively, in full accordance with the literature data on the order of stability of HPAs [17].

The acidic properties of the catalysts supported on γ -Al₂O₃ and SiO₂ were characterized by the TPD method. The TPD curve for the PMo–SiO₂ sample exhibits a peak at 156°C; in the case of PMo/Al₂O₃, the peak is shifted to higher temperatures (200°C); this

fact suggests that the latter catalyst contains stronger acid sites. The total acidity for the PMo/Al₂O₃ and PMo–SiO₂ samples is 65 and 59 μ mol NH₃/g_{cat}, respectively. For comparison, similar measurements were conducted for pure supports. It was found that the feed SiO₂ sorbs ammonia at a level of about 20 μ mol/g; that is, the immobilization of an IL leads to an increase in the number of acid sites (most probably, Brønsted sites) on the surface. At the same time, the total acidity of pure Al₂O₃ is 285 μ mol/g; the TPD curve exhibits a peak at 220°C. Thus, the deposition of an IL onto the surface of this support leads to a significant (fourfold) decrease in acidity.



Fig. 2. SALDI mass spectra of (a) PTA, (b) the $PW-SiO_2$, and (c) PW/Al_2O_3 catalysts recorded in the negative ion detection mode.

Comparison of the Activity and Stability of the Catalysts in Thiophene Oxidation

864

To determine the activity and stability of the synthesized catalysts, a set of tests on the oxidation of the model substrate—thiophene—was conducted. According to the literature [5, 19–23], thiophene oxidation occurs in accordance with Scheme 4 (see below) through the intermediate formation of sulfoxide and sulfone.



Scheme 4. Thiophene oxidation under the action of hydrogen peroxide.

The reaction can occur to form a sulfate anion and benzoic acid or, in the case of deeper oxidation, carbon dioxide. Data on the activity of the synthesized catalysts in model mixture 1 are shown in Table 1 and Fig. 4.

To avoid a deep oxidation of thiophene (to CO_2 and H_2SO_4), the $[H_2O_2]$: [S] molar ratio of 5 was used at the initial stage. However, Fig. 4 shows that, under these conditions, the maximum thiophene conversion did not exceed 65%. To reveal the cause of cessation of the reaction, the organic and aqueous phases of the reaction solution were analyzed by various methods. According to proton magnetic resonance (PMR) and C^{13} NMR, the organic phase contained only the feed thiophene and the solvent. ESI mass spectrometry analysis did not reveal the presence of carboxylic acids-possible products of the reaction occurring via the styrene formation pathway—in the aqueous phase. The addition of barium chloride to the aqueous phase led to the formation of a white precipitate of sulfate and, possibly, barium carbonate. The results suggest that, under these conditions, thiophene undergoes deep oxidation, which, according to the reaction stoichiometry, requires at least a tenfold excess hydrogen peroxide with respect to thiophene. It should be noted that, in this set of experiments, identical weighed portions of the catalysts were used to determine the possible contribution of the acidic properties of the support to the catalytic activity of the synthesized samples. This assumption follows from analysis of the literature data [5, 23]. In fact, it is known that Brønsted acid sites have a positive effect on thiophene derivatives in the case of heterogeneous catalytic oxidation [23]. In addition, the introduction of acids (most commonly, formic or acetic) to the reaction solution contributes to the occurrence of a deeper process in homogeneous or biphasic systems [24, 25]. However, Table 1 and the TPD data show that a change in the acidic properties did not have a significant effect on the activity of the samples; this finding suggests that the nature of the anion plays the dominant role in catalysis over immobilized ILs.

Figure 3 shows that the highest activity in the first cycle was exhibited by the PMo/Al_2O_3 catalyst synthesized by adsorption. However, after testing this sample in several consecutive cycles, the thiophene conversion significantly decreased, while the $PMo-SiO_2$ catalyst was found to be much more stable. The PW/Al_2O_3 catalyst exhibited fairly high stability; moreover, in the second cycle, the activity of this sample considerably increased; this finding suggests that the catalyst underwent conditioning. This effect also took place for the catalysts synthesized by covalent bonding; however, it was less pronounced.

Of two tungsten catalysts, the PW/Al_2O_3 catalyst provided a lower reaction rate in the first cycle. This result could be attributed to the fact that the tungsten content in this sample is lower than that in the PW–



Fig. 3. Stability of the catalysts immobilized on Perlkat and γ -Al₂O₃ in three consecutive cycles. Initial process conditions: $m_{cat} = 0.08 \text{ g}$, $[\text{H}_2\text{O}_2] : [\text{S}] = 5, 3 \text{ h}, 60^{\circ}\text{C}.$

SiO₂ catalyst (Table 1). On the other hand, according to Table 1, the PMo/Al₂O₃ catalyst contained a minimal amount of Mo (2 wt %); however, it was more active than the PMo–SiO₂ catalyst with a significantly higher metal content. This effect—the inverse effect of molybdenum content in heterogeneous composites on their activity in the oxidation of thiophene derivatives—is known from the literature [26]. Apparently, a high metal content accelerates the hydrogen peroxide decomposition, which is a process that competes with the target reaction.

The effect of temperature on the thiophene oxidation rate is also complex. This dependence was studied in a range of $50-70^{\circ}$ C using the example of the PMo/Al₂O₃ catalyst; it was found that the thiophene conversion achieves a maximum at $60-65^{\circ}$ C. This dependence can be attributed to the fact that, at a low temperature, the catalyst cannot exhibit an optimum activity, while a high temperature leads to an increase in the oxidizer decomposition rate. An optimum process occurs in a narrow temperature range.

To provide a more complete conversion of thiophene, a 50% H_2O_2 solution was used at a molar ratio with thiophene of about 10. To decrease the possible effect of the side reaction— peroxide decomposition— and increase the efficiency of use of H_2O_2 , it was charged in batches (0.4 mL + 0.4 mL after 3 h). This technique is known in the literature on the peroxide-mediated oxidation of various substrates [27, 28]. Our data are shown in Table 2.

It is evident from the table that the charging of H_2O_2 in batches was efficient: it provided an increase in the thiophene conversion almost to 90%.

The catalyst activity in petroleum feedstocks is shown in Table 3. The catalysts supported on γ -Al₂O₃ proved to be the most active in the oxidation of the diesel fraction. The highest activity was exhibited by

Table 2. Total conversion of thiophene (%) for the different modes of peroxide charging (10 mL of a thiophene solution in isooctane, 0.08 g of the catalyst, 0.8 mL of 50% H_2O_2)

| | Thiophene conversion, % | | | | | |
|---------|-----------------------------------|--|-----------------------------------|--|--|--|
| Time, h | PMo–SiO ₂ | | PW-SiO ₂ | | | |
| | $0.8 \text{ mL of H}_2\text{O}_2$ | $0.4 \text{ mL} + 0.4 \text{ mL} \text{ of } H_2O_2$ | $0.8 \text{ mL of H}_2\text{O}_2$ | $0.4 \text{ mL} + 0.4 \text{ mL of H}_2\text{O}_2$ | | |
| 1 | 45 | 40 | 52 | 47 | | |
| 3 | 58 | 69 | 69 | 70 | | |
| 6 | 66 | 86 | 75 | 88 | | |

Table 3. Total conversion of sulfur-containing derivatives (%) in petroleum feedstocks (Mo(W) : H_2O_2 : S molar ratio of 1 : 6 : 100)

| Catalyst | Conversion in diesel fraction | Conversion in synthetic crude oil |
|------------------------------------|-------------------------------|-----------------------------------|
| PMo-SiO ₂ | 42 | 85 |
| PW–SiO ₂ | 50 | 73 |
| PMo/Al ₂ O ₃ | 86 | 82 |
| PW/Al ₂ O ₃ | 64 | 47 |

the PMA-based catalyst with a low metal content on the surface.

In the case of an oil shale extract, the catalysts based on molybdenum derivatives showed the best results, regardless of the nature of the mineral support. In general, comparison of the model solutions shows that all of the catalysts, except for PW/Al_2O_3 , exhibit high activity in synthetic crude oil derived from oil shale. This feature of this model mixture is apparently associated with the structure of organic sulfur compounds contained in it. In fact, the oil shale was processed at high temperatures in the absence of oxidizers, such as atmospheric oxygen. Under these conditions, thiophenic compounds can undergo partial conversion to respective sulfides, which are much more readily oxidized by hydrogen peroxide in the presence of Mo- and W-containing catalysts [5, 16].

Thus, comparative analysis of the catalysts based on immobilized metal-containing ILs has shown that the order of catalyst activities is determined by the nature of the substrate. At a high content of thiophene or thiophene derivatives (model mixtures 1, 2), the best results in the first cycle are shown by the aluminasupported PMA-based PMo/Al₂O₃ catalyst synthesized by the adsorption method. This catalyst contains a minimum amount of the metal in the form of anions, which are PMA fragments comprising up to six Mo atoms. However, the stability of this catalyst is low. The PTA-based catalysts containing large fragments of heteropoly anions are more stable. In addition, the PMA-based catalyst synthesized by covalent bonding, which comprises polymolybdates formed as a result of HPA degradation during synthesis, is also stable; however, it is less active.

ACKNOWLEDGMENTS

The authors thank A.O. Chizhov for assistance in recording and interpreting mass spectrometry data.

This work was supported by the Russian Foundation for Basic Research, project no. 15-03-01995; OOO NIKSA; and Gercelia Limited.

REFERENCES

- 1. Supported Ionic Liquids: Fundamentals and Applications, Ed. by R. Fehrmann, A. Riisager, and M. Haumann (Wiley–WCH, Weinheim, 2014).
- 2. M. Li, M. Zhang, A. Wei, et al., J. Mol. Catal. A: Chem. **406**, 23 (2015).
- X. Y. Shi and J. F. Wei, J. Mol. Catal. A: Chem. 280, 142 (2008).
- 4. E. Kowsari, *Ionic Liquids: New Aspects for the Future*, Ed. by J.-I. Kadokawa (InTech, Rijeka, 2013), ch. 11, p. 277.
- A. V. Anisimov and A. V. Tarakanova, Ross. Khim. Zh. (Zh. Ross. Khim. Ob-va Im. D.I. Mendeleeva) 52 (4), 32 (2008).
- X. Shi, X. Han, W. Ma, et al., J. Mol. Catal. A: Chem. 341, 57 (2011).
- J. Zhang, A. Wang, X. Li, and X. Ma, J. Catal. 279, 269 (2011).
- 8. I. G. Tarkhanova, A. V. Anisimov, S. V. Verzhichinskaya, et al., Pet. Chem. 56, 158 (2016).
- S. Otsuki, T. Nonaka, N. Takashima, et al., Energy Fuels 14, 1232 (2000).
- I. G. Tarkhanova, M. G. Gantman, and V. M. Zelikman, Appl. Catal., A 470, 81 (2014).
- 11. X. Y. Shi and J. F. Wei, J. Mol. Catal. A: Chem. **280**, 142 (2008).
- 12. Y. Sasaki, K. Ushimaru, K. Iteya, et al., Tetrahedron Lett. 45, 9513 (2004).

- 14. A. I. Busev, *Analytical Chemistry of Tungsten* (Nauka, Moscow, 1976) [in Russian].
- 15. A. K. Buryak and T. M. Serdyuk, Usp. Khim. 82, 369 (2013).
- 16. S. V. Kardashev, S. V. Lysenko, S. V. Egazar'yants, et al., Khim. Tekhnol. Topl. Masel, No. 6, 3 (2015).
- 17. I. V. Kozhevnikov, Chem. Rev. 98, 171 (1998).
- 18. J. L. Garsia-Gutierrez, G. A. Fuentes, M. E. Hernandez-Teran, et al., Appl. Catal., A **334**, 366 (2008).
- 19. J. T. Sampanthar, H. Xiao, J. Dou, et al., Appl. Catal., B 63, 85 (2006).
- L. Chen, S. Guo, and D. Zhao, Chin. J. Chem. Eng. 15, 520 (2007).
- 21. B. Zhang, Z. Jiang, J. Li, et al., J. Catal. 287, 5 (2012).

- 22. L. Kong, G. Li, and X. Wang, Catal. Lett. 92, 163 (2004).
- 23. L. Kong, G. Li, and X. Wang, Catal. Today **93**, 341 (2004).
- 24. S. Otsuki, T. Nonaka, N. Takashima, et al., Energy Fuels 14, 1232 (2000).
- 25. F. Al-Shahrani, T. Xiao, S. A. Liewellyn, et al., Appl. Catal., B **73**, 311 (2007).
- D. Wang, E. W. Qian, H. Amano, et al., Appl. Catal., A 253, 91 (2003).
- 27. Y. Bi, M. Zhou, H. Hu, et al., React. Kinet. Catal. Lett. **72**, 73 (2001).
- Z. P. Pai, D. I. Kochubey, P. V. Berdnikova, et al., J. Mol. Catal. A: Chem. 332, 122 (2010).

Translated by M. Timoshinina