JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 4, April 2009, p. 502 - 508

Polyaniline protonated with heteropolyacids as organic-inorganic hybrid materials for catalytic conversion of ethanol

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PANI supported heteropolyacids (HPAs) $H_3[PMo_{12}O_{40}]\cdot xH_2O$ (HPMo) and $H_4[PMo_{11}VO_{40}]\cdot yH_2O$ (HPVMo) were prepared, characterised and tested as catalysts for ethanol conversion. Supported and unsupported samples were characterised by nitrogen physisorption, SEM, thermal analysis and FT-IR spectroscopy. The thermal decomposition of PANI support started at ca. 673K, while for PANI-supported HPAs a decrease of decomposition temperature are observed. The reaction rates of ethanol conversion and acetaldehyde formation increased on PANI supported HPAs comparatively with pure HPAs. The values of apparent activation energies in case of PANI-supported catalysts have lower values as the unsupported HPAs for acetaldehyde formation. A "compensation effect" was evidenced for acetaldehyde and ethylene formation.

(Received August 19, 2008; accepted April 23, 2009)

Keywords: Polyaniline, Heteropolyacids, Texture, Structure, Ethanol, Catalytic conversion

1. Introduction

Mo- and V-containing heteropolyacids with Keggin structure exhibit a special interest for heterogeneous catalysis owing to their high acid strength and also oxidizing properties [1-5]. Pure HPAs generally show low catalytic reactivity owing to their small surface area. In order to be more effective for catalytic reactions, HPAs are usually impregnated on different porous materials [6-16] and polymers [17-22].

Most frequently used are molybdophosphoric acid $H_3[PMo_{12}O_{40}]\cdot xH_2O$ (HPMo) and 1-vanado-11-molybdophosphoric acid $H_4[PMo_{11}VO_{40}]\cdot yH_2O$ (HPVMo) in consequence of their high catalytic activity in the selective oxidation of unsaturated aldehydes and the oxidation of low alcohols [3-5, 23-27].

Polymer materials have been widely used in chemical reactions as supports or catalysts due to their flexible applicability. Conducting polymers such as polyaniline, polypyrrole and polythiophene, with immobilised catalytic sites, have attracted much interest because these kinds of substances are able to replace the catalyst based on organic ligands, such as porphyrins, as a catalyst in many reactions due to its higher resistivity in oxidizing environments [28]. Polyaniline (PANI) is a conductive polymer, is cheap and stable to heat and air atmosphere. It is also the first commercially available conducting polymer. Polyaniline (PANI) is the simple 1,4 coupling product of monomeric aniline molecules, with the general formula:

$$-[(B\text{-}NH\text{-}B\text{-}NH)_y\,(B\text{-}N{=}Q{=}N)_{1-y}]_n-$$

Were B is the benzene ring, and Q represents the quinoine ring and *y* is the degree of oxidation $(0\le y\le 1)$ defines the oxidation state of the polymer. Oxidation state (1-y), can be continuous modified beginning with 0, for the entire reduced polymer (leucoemeraldine), until 0.5 when forms the half oxidised polymer (emeraldine) or until 1 for the entire oxidised polymer (pernigraniline) [29]. The PANI forms with $y\neq 0$ can be protonated by non-oxidizing acids, the protonation take place on the imine nitrogen atoms [30].

The synthesis and the characterisation of PANI doped with different anions are critical since many properties of the final polymer are greatly influenced by the nature of the doping ion, properties that provide the special destination of it. The first attempt of the electrocatalytic application of PANI was mentioned by Keita et al [31] and Bidan et al [32] by incorporation of Keggin type heteropolyanions into PANI. M.Hasik et al [17] show that PANI base can be used as convenient catalytic support on which non-oxidising heteropolyanions can be dispersed via protonation. This protonation reaction results in the formation of an ionic bond between heteropolyanions and the support and should also modify the acid-base properties of the catalyst.

HPAs catalysts immobilized on conjugated conducting polymers have found successful applications as heterogeneous catalysts in some vapor-phase reactions such as ethanol and 2-propanol conversion [17, 19, 21] and hexanol conversion [22]. The type of carrier, textural and structural properties influence the thermal stability and the catalytic activity of Keggin-type heteropolyacids.

In order to obtain highly dispersed heteropolyacids species, $H_3PMo_{12}O_{40}$ and $H_4PVMo_{11}O_{40}$ were supported on polyaniline (PANI). Ethanol conversion was selected as a test reaction to characterise PANI supported HPAs. By this reaction could be evaluate the prevailing character (acidic or redox) of the heteropolyacids type catalysts. The goal of this work was to characterise the thermal stability, textural properties and catalytic activity of PANI-supported heteropolyacids in reference to the bulk solid heteropolyacids.

2. Experimental

H_4 $[PMo_{11}VO_{40}]\cdot 12H_2O$ was prepared by two methods: Tsigdinos method (ether extraction from HPVM solution) and hydrothermal method (preparation of HPVMo from the constituent acids at 353 K) [33-34]. In both cases HPAs were crystallized slowly from aqueous solutions at room temperature. $H_3[PMo_{12}O_{40}]\cdot 13H_2O$ was purchased from Merck. The as-received material was recrystallized prior to use. They are stable at room temperature with 12-14 H_2O molecules.

Polyaniline (PANI) with incorporated heteropolyanions was prepared by using a two-step reaction. This method involved synthesis of polyemeraldine base by polymerization of aniline with $(NH_4)_2S_2O_8$ in HCl followed by deprotonation with ammonia [15-18]. The HPAs active phase deposition on the PANI support was performed by protonation from water : ethanol = 1:1 solution. The HPMo and HPVMo acids were deposited by protonation in the concentration of 16.6 wt. % loading.

The structure and texture of $H_3PMo_{12}O_{40}$ and $H_4PVMo_{11}O_{40}$ supported on polyaniline was studied by FT-IR, low temperature nitrogen adsorption and scanning electron microscopy with EDS analysis. Thermal stability of both HPAs supported on polyaniline was studied by TG and DSC measurements.

The IR absorption spectra were recorded with a Jasco 430 spectrometer (spectral range 4000-400 cm^{-1} range, 256 scans, and resolution 2 cm^{-1}) using KBr pellets.

Textural characteristics of the outgassed samples were obtained from nitrogen physisorption using a Micrometrics ASAP 2000 instrument. The specific surface area S_{BET}, mean cylindrical pore diameters d_p and adsorption pore volume V_{pN2} were determined. Prior to the measurements the samples were degassed to 10^{-5}Pa at 423K. The BET specific surface area was calculated by using the standard Brunauer, Emmett and Teller method on the basis of the adsorption data. The pore size distributions were calculated applying the Barrett-Joyner-Halenda (BJH) method to the desorption branches of the isotherms. The IUPAC classification of pores and isotherms were used in this study.

Microstructure characterisation of the catalyst particles was carried out with a JEOL JSM 6460 LV instrument equipped with an OXFORD INSTRUMENTS EDS analyser. Powder materials were deposited on adhesive tape fixed to specimen tabs and then ion sputter coated with gold.

Thermogravimetric analysis was performed on a Netzsch TG 209 derivatograph and on Netzsch DSC 204**.** The working conditions were as follows: samples amount 30-50mg for the supported samples; platinum crucible, heating rate 2.5K/min, 5K/min and 10K/min; nitrogen atmosphere.

Catalytic experiments were carried out using a pulse microreactor, with a 0.7 ml of catalyst, in the temperature range 463-563K. Six pulses of 3 μl of C_2H_5OH ($2{,}4\cdot 10^{-3}$g ethanol corresponds to 58.25 μmol) were introduced within 20 min. The products were analyzed by two gas chromatographs Chromatron GCHF 18.3 type with columns filled with Porapak QS (80-100 mesh) using TCD and FID detectors. The carrier gases (Ar and N_2) flow were kept constant at 25 ml/min. The reoxidation process was realized in an air flow during 2 h, at the same temperature used for fresh catalysts test. The catalysts were thermally pretreated in carrier gas flow (60 ml/min) up to the tested temperature prior to the reaction with organic reactant.

3. Results and discussion

In order to confirm the presence of the Keggin anion on PANI, the supported HPAs samples were analysed by FTIR. In the IR spectra of PANI sample a strong band at 1164 cm^{-1} is observed, this band being attributed to non-protonated base form [14, 18]. In the IR spectra of PANI supported HPAs this band became weak (shoulder), and another strong band characteristic of the protonated states appeared at 1142 cm^{-1} in both HPMo and HPVMo catalysts. In PANI supported HPAs samples, the specific absorption bands of the Keggin structure bands are broadened and partially obscured because of the strong absorption bands of PANI (not shown). By comparison with those of unsupported HPAs the Keggin type characteristic IR bands of HPAs in PANI supported samples were observed at shifted positions. These results confirm that HPAs were supported on the PANI matrix as a charge-compensating component.

Characteristic parameters of the texture of PANI supported HPAs catalysts determined by BET measurements are summarized in Table 1. For both HPMo/PANI and HPVMo/PANI one observe a type II isotherm with a type H3 hysteresis loop in the high range of relative pressure. Hysteresis loop H3 type shows that HPA/PANI samples consists of aggregates of plate-like particles, which possess non-rigid slit-shaped pores, which was confirmed by SEM analysis [14].

The specific surface area of PANI is 35 m^2/g, and the values of specific surface areas of HPAs deposited on PANI are approximately the same: 38 m^2/g for HPMo and to 37 m^2/g for HPVMo respectively (Table I). The specific surface area of both HPAs supported on PANI increases slightly comparatively with the dedoped PANI, so the specific surface area could be assumed to be given by the support.

The mean pore diameter (d_m) varies from 45 nm for PANI support to 34 nm and 41 nm for PANI supported HPMo and HPVMo respectively, as one results from the pores size distribution curves. The decreasing of pore diameter for PANI supported HPAs could be explain owing to support pores blocking by active phase, as well as by the formation of some HPAs crystallites agglomeration.

Table 1 Characteristic parameters of the texture of pure HPAs and PANI-supported HPAs samples.

Sample Characteristics	HPMo	HPVMo	HPMo/PANI	HPVMo/PANI	PANI
S_{BET} (m^2/g)	4	4	38	37	35
Pore volume,V_{pN2} (cm^3/g)	0.01	0.01	0.11	0.14	0.19
Pore diameter, d_m (nm)	14	12	34	41	45
HPAs, wt %	-	-	16.6	16.6	-

The morphology of pure HPMo and HPVMo illustrated by SEM analysis shows that it consists of agglomerates of irregular crystallites varying in size and habit. PANI support is composed of agglomerates of irregular shape particles with an average diameter below 0.5 µm and a marked polydispersity in size (not shown). The surface morphology of PANI-supported HPAs is practically identical to that of the pure polymer. From SEM images one can see that no separate crystallites of the bulk phase of HPAs were found in the supported samples.

Thermal behaviour of the pure HPMo and HPVMo heteropolyacids, respectively HPMo/PANI and HPVMo/PANI was studied comparatively. The two pure HPAs are stable as anhydrous species within the range of temperature 423 – 553K for HPVMo and 423 – 653K for HPMo. Above these temperature, HPA decomposes losing the constitutive water and transform into correspondent oxides [12, 35-37].

The HPAs deposited on the support have a different behaviour than that of the pure HPAs in the range of low and high temperatures. The thermal curves of both HPAs supported on PANI did not show the effects characteristic of parent acids and resembled the thermal curve of pure PANI. The thermal curves of PANI and PANI supported HPAs exhibit only two processes, the hydrated water elimination in one or two steps and the decomposition of the polymer.

Thermogravimetric curves TG and DTG of polyaniline show a decrease of mass (ca. 5%) within the temperature region 323-423K and two endothermic DTG peaks at 323 and 368K. The weight changes in this region are associated with release of solvents and water from the samples. After a further slight loss, the mass of the PANI sample became relatively constant in the temperature region 473-633K. The DTG curve shows that the decomposition process of PANI backbone chains started at ca. 673K and the minimum of endothermic DTG peak appear at 783K (Table 2).

The decomposition of PANI supported HPAs take place with a maximum decomposition rate (T_{vmax}) at lower temperature than for PANI support (endothermic DTG peak at 733K for HPVMo and at 708K for HPMo). The same observation results from DSC curves examination. The DSC exothermic peaks corresponding to decomposition temperature of PANI supported HPAs are below the PANI support one [14].

Table 2. Thermogravimetric data for PANI and supported samples.

Sample	$T_{5\%}$, K*	T_{desc}, K**	T_{vmax}, K***	Δm_{Tvmax}, %****
PANI	418	673	783	15.2
HPMo/PANI	410	605	708	19.4
HPVMo/PANI	411	628	733	20.5

* represents the temperature at 5% weight loss of the samples
** the onset decomposition temperature
*** temperature at which decomposition rate is maximum
**** the weight loss at temperature at which decomposition rate is maximum

The catalytic experiments of supported and unsupported heteropolyacids were carried out for ethanol conversion using a pulse method. The reaction products obtained on acid (dehydration) catalytic centres were ethylene (ET) and diethyl ether (DEE), and respectively acetaldehyde (ACA) which was obtained on redox (dehydrogenation) catalytic centres. In the pulses leaving the reactor were detected also water, unreacted alcohol and, especially at higher temperatures, minor quantities of CO_x. As water gives a large diffuse peak, it is not suitable for quantitative determination.

The conversion of ethanol is acid-catalysed reaction, with the formation of ether resulting from a bimolecular mechanism that involves physically adsorbed alcohol and "chemically activated" alcohol. Olefin formation occurs through a unimolecular mechanism predominantly in the bulk of HPAs crystallites, while diethyl ether is formed on their external surface [24].

For both supported and unsupported HPAs catalysts, the sum of the reaction products and the unreacted alcohol is always smaller than the amount of alcohol introduced onto the catalyst. The same behavior was also observed in the case of the $H_4SiW_{12}O_{40}$ catalyst. Bilelanski et al. showed that such results are due to the partially irreversibly sorbtion of the alcohol by the solid HPAs [26].

Ethanol conversion over both HPAs catalysts decreases with pulse number and the conversion over HPMo has lower values than for HPVMo catalyst. For PANI-supported catalysts the values of ethanol conversion are lower in comparison with pure HPAs ones (Fig. 1). After reoxidation, values of ethanol conversion are comparable with these obtain after first cycle of reduction for all tested catalysts. Ethanol conversion over PANI-supported catalysts decreases with pulse number, and the conversion over supported HPVMo appeared to be somewhat similar to supported HPMo ones (Fig. 1).

The ethylene and diethyl ether quantities over both pure heteropolyacids remain nearly constant with the increasing of pulse number after the second pulse. The values of DEE quantities reach 10 micromoles at 523 K, while for ethylene the maximum of quantity (20 micromoles) is reached at 563 K. The acetaldehyde amount increased gradually with pulse number from 2 to 9 micromoles at 543 K and 563 K for both pure HPAs.

In the case of PANI-supported catalysts the reaction products are acetaldehyde and ethene, while ethyl ether is not detected. Comparably with supported HPMo, the amounts for ethene are quite similar over supported HPVMo. For both supported catalysts the ethylene quantity decreased continuously with pulse number. At 503 K, the yield of ethylene reach a maximum of 1 micromoles at first pulse for both PANI supported HPAs. Acetaldehyde which is known to be produced on redox centres results in significant amount for both supported catalysts. However, supported HPVMo led to higher quantities of ACA, especially at 503 K. ACA quantities decreased with the pulse number for both supported catalysts and after sixth pulse its values present still relatively high values (Fig. 2b).

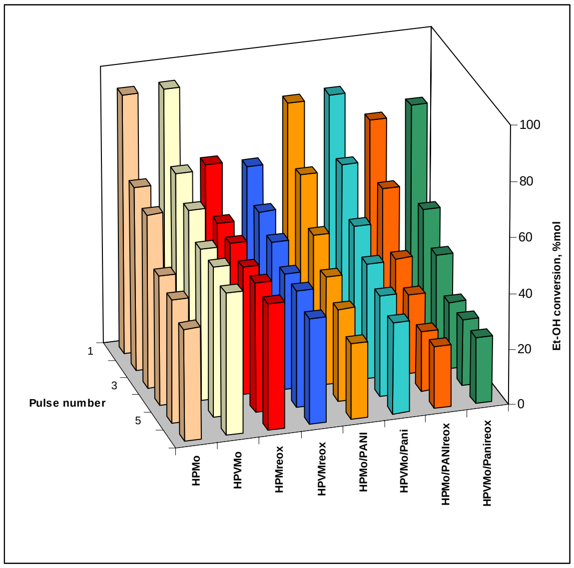
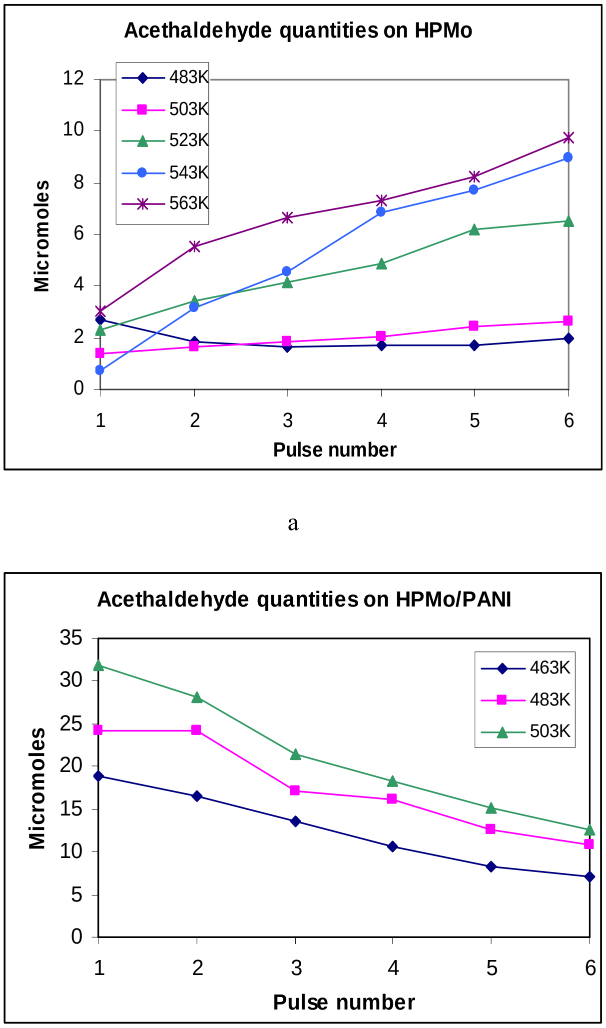


Fig. 1. The conversion of ethanol as a function of reactant pulses at 503K for supported and unsupported catalysts

The reaction rates corresponding to the transformation of ethanol and formation of acetaldehyde, respectively, increased on fresh PANI-supported HPAs comparatively with unsupported HPAs ones in the whole range of temperatures: 463-503 K (Table 3). Thus, the very high dispersion of the HPAs yielded an active catalyst for this reaction and especially for acetaldehyde formation. In contrast, the reaction rates of ethylene present lower values for PANI-supported HPAs comparatively with unsupported HPAs ones.

After reoxidation, as a result of enriching catalyst surface with oxygen, the values of reaction rates of acetaldehyde formation for PANI-supported catalysts are near the same as for fresh catalysts.



a

b

Fig. 2. Quantities of acetaldehyde as a reaction product for ethanol conversion on pure HPMo (a) and PANI-supported HPMo (b)

The catalytic activities of supported and unsupported HPAs, fresh and reoxidated samples were compared on the basis of reaction rates per gram catalyst [(mol reaction product)·$(g_{cat})^{-1}$ ·s^{-1}]. The resulting reaction rates for acetaldehyde formation are presented in Table 3 and as ln r vs. 1/T in Figure 3. It could be observed that reaction rates values show that the PANI-supported catalysts (open symbols), both fresh and after reoxidation appeared to be far more active than bulk HPMo and HPVMo catalysts (filled symbols) in dehydrogenation reaction.

Table 3. Reaction rates of reaction products formation at different temperature for PANI-supported and unsupported heteropolyacids

Sample	**Average rates of reaction products formation ×10^6, mole/g·s**										
	r_{ACA}				**r_{ET}**				**r_{DEE}**		
	463K	**483K**	**503K**	**523K**	**463K**	**483K**	**503K**	**523K**	**483K**	**503K**	**523K**
HPMo	-	2.37	3.56	6.19	-	5.99	7.50	12.41	10.61	6.57	10.59
HPVMo	-	2.48	2.98	7.09	-	2.10	6.71	14.97	6.55	7.07	12.13
HPMo-reox	-	3.82	5.38	6.50	-	4.78	5.31	12.32	6.21	4.68	10.07
HPVMo-reox	-	4.10	5.76	8.73	-	2.66	5.80	12.11	5.94	6.12	10.76
HPMo/ PANI	100.68	144.55	170.72	-	0.31	0.78	1.88	-	-	-	-
HPVMo/ PANI	105.63	153.65	195.70		0.16	0.72	1.89	-	-	-	-
HPMo/ PANI -reox	87.41	138.38	161.95	-	0.18	0.86	2.21	-	-	-	-
HPVMo/ PANI -reox	97.30	139.81	177.64	-	0.06	0.68	1.98	-	-	-	-

Table 4. The kinetic data for acetaldehyde formation on PANI-supported and unsupported heteropolyacids.

Sample	Temperature (K)	Fresh catalysts			After reoxidation		
		r_{ACA}×10^6 (mol·g^{-1}·s^{-1})	E_a (kJ/mol)	A (s^{-1})	r_{ACA}×10^6 (mol·g^{-1}·s^{-1})	E_a (kJ/mol)	A (s^{-1})
HPMo	483	2.37	56.6	3.14×10^6	3.82	38.2	5.15×10^4
	503	3.56			5.38		
	523	6.19			6.50		
	543	13.67			12.23		
	563	14.89			14.11		
HPVMo	483	2.48	44.9	1.8×10^5	4.07	36.6	3.82×10^4
	503	2.98			5.76		
	523	7.09			8.73		
	543	8.76			9.48		
	563	10.55			16.18		
HPMo/ PANI	463	100.68	25.6	8.16×10^4	87.41	29.9	2.24×10^5
	483	144.55			138.38		
	503	170.72			161.95		
HPVMo/ PANI	463	105.63	29.8	2.55×10^5	97.30	29.1	1.95×10^5
	483	153.65			139.81		
	503	195.70			177.64		

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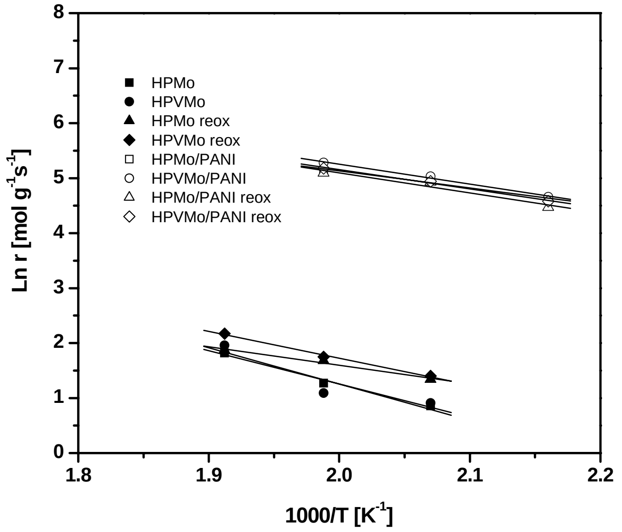


Fig. 3. Arrhenius plots of specific reaction rates of PANI-supported and unsupported heteropolyacids series for acetaldehyde formation.

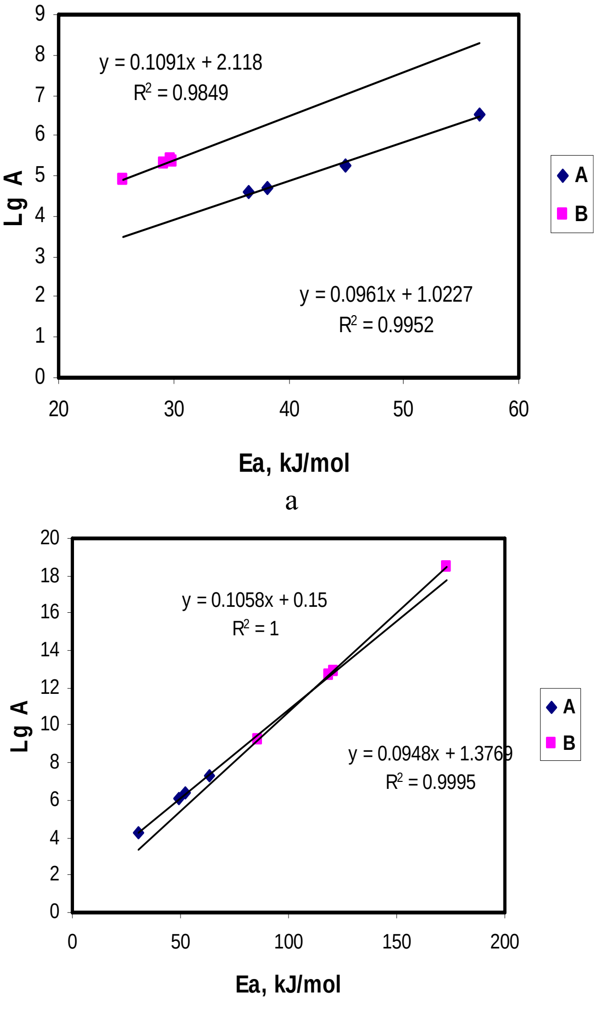
For bulk catalysts the values of apparent activation energies for all reaction products formation are smaller for HPVMo than for HPMo one. On the other hand apparent activation energies in case of PANI-supported catalysts have lower values as the unsupported HPAs for acetaldehyde and almost the same values for ethylene formation.

A comparison of the apparent activation energies of the tested catalysts for acetaldehyde formation reveals an important decrease in the case of PANI-supported heteropolyacids. Their values amounted to ca. 25-30 kJ·mole^{-1} for PANI-supported HPAs, while for parent acids the values are: 57 kJ/mole for HPMo, respectively 45 kJ/mole for HPVMo (Table 4). A "compensation effect" was evidenced from the relationship between pre-exponential factor A and apparent activation energies E_a for acetaldehyde and ethylene formation (Fig. 4).

On the basis of compensation effect it was calculated the isokinetic temperature T_i. Isokinetic temperature T_i has an important physical meaning. It represents a temperature at which all reactions of the series should proceed at the same rate. At this temperature all kinetic parameters of a reaction are equal. Isokinetic temperature is calculated by the equation:

$$T_i = \frac{1}{2.303 R \cdot a} \tag{1}$$

where “a” is the slope of the linear plots and R is the gas constant in the ideal gas equation (R = 8.31).



a

b

Fig. 4. Correlation between lg A vs. activation energy for acetaldehyde formation (a) and ethylene formation (b); A-the dots correspond to: HPMo, HPVMo fresh and reoxidated, B-the dots correspond to HPMo/PANI, HPVMo/PANI fresh and reoxidated..

The calculated isokinetic temperatures in the case of PANI supported HPAs were T_{i1}=479K for acetaldehyde formation and T_{i2}=494K for ethylene formation, respectively. It was obtained almost the same T_i values for both reaction products: acetaldehyde and ethylene.

4. Conclusions

Protonation of polyaniline with 12-molybdo-phosphoric acid and 11-molybdo-1-vanado-phosphoric acids can be used as a convenient preparation method of polymer supported catalysts.

FT-IR studies showed that HPAs anions preserved their Keggin structure after deposition on polyaniline support. The specific surface area of both HPAs supported on PANI increases slightly comparatively with the dedoped PANI, so the specific surface area could be assumed to be given by the support.

The surface morphology of the PANI-supported samples is almost similar to that of PANI support, and thereby a relatively uniform distribution of active phase in the support pores is observed. The thermal stability of PANI-supported heteropolyacids is given by thermal stability of the PANI support.

Between 463 and 503K the reaction rates of ethanol transformation and formation of acetaldehyde increased on PANI-supported HPAs comparatively with pure HPAs. High dispersion of the HPAs yielded an active catalyst for this reaction and especially for acetaldehyde formation. The values of apparent activation energies for all reaction products formation are smaller for HPVMo than for HPMo one. On the other hand apparent activation energies in case of PANI-supported catalysts have lower values as the unsupported HPAs for acetaldehyde formation. A "compensation effect" was evidenced for acetaldehyde and ethylene formation.

Acknowledgment

These investigations were partially financed by the Ministry of Education and Research of Romania Grant No 78 GR/2007.

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