



## Controlled nitration of anisole over $\text{HNO}_3/\text{PO}_4/\text{MoO}_3/\text{SiO}_2/\text{solvent}$ systems



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### ABSTRACT

Nitroanisoles have wide applications in pharmaceuticals, perfumery and production of corresponding amines used extensively in dye industry. The presence of activated methoxy group in the aromatic ring, causes the nitration of anisole to be complex and difficult to control. The catalysts obtained by mixing phosphoric acid with ammonium molybdate, and impregnating the solution on silica gel, are composed of  $\text{PO}_4^{3-}$  ions built in the structure of surface  $\text{Mo}_\infty\text{O}_{3\infty}$  lattice (heteropolyanion structure-like species). Using various amounts of the molybdenum species, it is possible to manipulate the catalyst acidity and simultaneously its activity. At room temperature, for 30 min with using fuming nitric it is possible to obtain ca. 90% anisole conversion with 62% selectivity to 4-nitroanisole. When 65%  $\text{HNO}_3$  is used, the conversion decreases to 76%, however the selectivity to 4-nitroanisole increases to 74%. Another advantage of the obtained catalysts is the possibility of their effective reuse in the subsequent reactions.

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### 1. Introduction

Methoxy group in aromatic ring belongs to the activating for electrophilic substitution groups [1]. For example, the group is so activating that methoxybenzene (anisole) reacts even with bromine itself, and if excess of bromine is used, the tribromide is readily generated. Despite of these facts, nitration of anisole is complex and difficult to perform [2]. This is because the aromatic nucleus is activated towards attack by the electrophilic species and in the concentrated nitric acid the reaction is rapid and exothermic which leads to polynitrated compounds. On the other hand, application of diluted nitric acid leads to formation of large amounts of by-products, because the aromatic ring is more likely to be oxidatively cleaved. For these reasons it is necessary to select the appropriate nitrating mixture (a nitrating agent and an acid catalyst) allowing effective and controlled nitration.

Hoggett et al. discussed application of various nitration mixtures for anisole nitration, including nitric and sulfuric acids, nitric acid with acetic acid, benzoyl nitrate and acetyl nitrate [3]. The obtained specific selectivity to 2-nitroanisole (even 70% in the reaction with acetyl nitrate) was rationalized in terms of an initial interaction between the nitronium ion and the *n*-donor oxygen atom, *i.e.* the initial attack of the nitrating species takes place at oxygen in  $\text{OCH}_3$

group and is followed by an intramolecular rearrangement to the 2-nitro-compound. Afterwards, the same authors gave another explanation, *i.e.* the higher selectivity to 2-nitroanisole is due to the formation of hydrogen-bonded anisole molecules in acidic solutions [4] and through selection of the concentration of nitrating mixture (*e.g.* nitric and sulfuric acids concentrations) it is possible to obtain 30–60% 2-nitroanisole in the product. Moreover, it was shown that the nitration with 40%  $\text{HNO}_3$  in the presence of some nitrous acid yielded 2,4-dinitrophenol as a main product. Olah et al. [5] studied application of nitronium salts,  $[\text{NO}_2^+\text{BF}_4^-]$  and  $[\text{NO}_2^+\text{PF}_6^-]$ , and obtained high 2-nitro/4-nitroanisole ratio of 2.67 and 2.41, respectively. The authors suggest that in the intermediate methylphenylnitronium ion,  $\text{C}_6\text{H}_5(\text{CH}_3)\text{O}^+\text{NO}_2$  (formed after initial attack on oxygen), nitro group transfers only intermolecularly, because the intramolecular process is symmetrically forbidden and would necessitate a strained four-center transition state. Thus, the isomer distribution properly reflects the electronic effects of the strongly electron-donating methoxy group. Thompson and Zeegers [6] proposed two-phase nitration procedure in the presence of nitric acid, organic solvent (diethyl ether) and sodium nitrite. It was determined that the concentration of nitric acid is a very important factor: when 70%  $\text{HNO}_3$  was used, the main product was 2,4-dinitroanisole, whereas using 30%  $\text{HNO}_3$  did not give any nitrated product even after 24 h. As the amount of nitrite increases, the amount of 2-nitroanisole decreases. The authors proposed that anisole nitration does not undergo *via* phenoxy radical mechanism but by electrophilic nitration assisted by N(III) species. Anisole was

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also nitrated by charged-transfer mechanism in the presence of tetranitromethane in acetonitrile [7].

Apart from different nitrating mixtures, application of solid acid catalysts in anisole nitration were also described. Solid catalysts meet the recent ecological and safety requirements, and they can be promising alternative to commonly used catalysts [8–13]. For example, in the presence of acidic montmorillonite clay impregnated with anhydrous cupric nitrate, nitroanisoles with 98% yield were obtained [8]. Great selectivity to 4-nitroanisole (80%) was obtained in the reaction with  $P_2O_5/SiO_2$  and fuming nitric acid [9]. Mesoporous silica impregnated with cesium exchanged Keggin type heteropolyacids (HPAs) were used as dispersed catalysts in the mixture of nitric acid (70%) and anisole [10]. The highest yield of nitroanisoles (ca. 60%) was obtained with cubic silica impregnated with cesium exchanged polyphosphotungstic acid after 24 h.

So far, the catalysts combining catalytic properties of  $P_2O_5/SiO_2$  (good selectivity [9]) with supported HPAs (high conversion and availability [10]) through mixing of phosphoric acid with ammonium molybdate, followed by impregnation of the obtained solution on the silica gel, and followed by heating, were successfully prepared. As a result, mixed catalysts composed of  $PO_4^{3-}$  ions built in the structure of surface  $Mo_{\infty}O_{3\infty}$  lattice (heteropolyanion-like species) were obtained. Using various amounts of the molybdenum species, it has been possible to simultaneously manipulate the catalyst acidity and activity.

To the best of my knowledge, there is still lack of reports on application of solid acids catalysts in anisole nitration, despite the fact that the products of anisole nitration are widely used in pharmaceutical, perfumery and dye industry. To fill this gap, in this work the application of solid catalysts for anisole mononitration under mild conditions without extra additives (e.g. nitrites) is fully described. Importantly, the obtained nitroanisoles are not contaminated with nitrophenols. Moreover, possible reaction mechanisms depending on various concentrations of nitric acid used are discussed. Conclusions from this work will be useful for both designing novel catalysts and choosing proper conditions for nitration of other activated aromatics.

## 2. Experimental

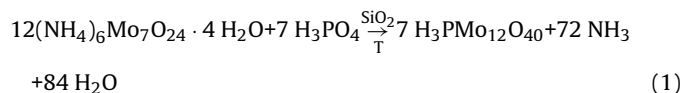
Phosphomolybdic acid hydrate was purchased from Sigma–Aldrich. Materials purchased from Avantor™ Performance Materials: anisole (pure), ammonium molybdate tetrahydrate  $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$  (pure), 1,2-dichloroethane (pure), phosphoric acid (85%, pure), magnesium sulfate anhydrous (pure), sodium hydrogen carbonate (pure). Silica gel ( $SiO_2$ ) was purchased from Mątwy, Poland. Fuming nitric acid was obtained in distillation from mixture of 65% nitric acid and 98% sulfuric acid.

Analysis of the reaction products was made using gas chromatography with a GC 17A, Shimadzu Corp. and a Rxi-5Sil MS ( $30m \times 0.32mm \times 1.0\mu m$ ) column. The sample of post-reaction mixture was dissolved in 1,2-dichloroethane. The quantitative composition was determined by internal standard method using peak areas and chlorobenzene as the internal standard (IS). The composition of the product was confirmed by GC/MS.

Raman spectra were recorded on a Nicolet Omega Dispersive Raman Spectrometer. Infrared spectra (IR) were recorded using Nicolet 6700 interferometer ( $4000-400\text{ cm}^{-1}$ , resolution  $4\text{ cm}^{-1}$ ) with ATR. X-ray powder diffraction patterns were recorded on a Bruker D8 Discover diffractometer. The solid-state  $^{31}P$  MAS NMR was performed on Bruker Avance II 500MHz spectrometer. The spinning frequency was 5kHz. All measurements were carried out at room temperature using  $P(Ph)_3$  as standard reference to obtain the chemical shift of the solid materials.  $^1H$  NMR spectra were recorded on Varian Mercury 400 spectrometer at room

temperature in  $CDCl_3$ . Textural properties of the catalysts surface were determined using a specific area analyzer of the surface and the microporosity Micromeritics Tristar II 3010. Adsorption/desorption experiments were made for dinitrogen within the  $p/p_0$  range of  $0.02-1.0$  at  $-196^\circ C$ . The acidity of the catalyst was determined by measurements of initial electrode potential and potentiometric titration method [14,15]. Certain 0.2g of catalyst was suspended in 25 mL of acetonitrile and the system was magnetically stirred for 1 h. The suspension was titrated with a solution of 0.01 N *n*-butylamine in acetonitrile. Then the variation in the electrode potential was measured with pH meter, using a standard glass electrode. This method enables determination of the total number of acid sites and their distribution.

*Preparation of P/Mo/SiO<sub>2</sub>.* The catalysts were prepared according to the scheme:



The solution of ammonium molybdate tetrahydrate and phosphoric acid in 3%  $H_2O_2$  was applied by wet impregnation method on  $SiO_2$  (grains 0.7–1.2 mm). Then, the catalysts were dried at  $150^\circ C$ . Next, it was heated at  $300^\circ C$  for ca. 16 h. To obtain 5 g of the catalysts, the amounts of substrates are as follows:

P/15Mo/Si – 0.92 g (0.7 mmol) of ammonium molybdate tetrahydrate, 7 mL of 3%  $H_2O_2$ , 4.25 g of  $SiO_2$ , 0.043 g (0.4 mmol) of  $H_3PO_4$ ,

P/45Mo/Si – 2.76 g (2.2 mmol) of ammonium molybdate tetrahydrate, 4.5 mL of 3%  $H_2O_2$ , 2.75 g of  $SiO_2$ , 0.13 g (1.3 mmol) of  $H_3PO_4$ .

*Nitration process.* 1,2-dichloroethane as a solvent (10 mL), the catalyst (1 g) and 0.3 mL (0.0069 mol) of fuming  $HNO_3$  or 0.5 mL (0.0069 mol) of 65%  $HNO_3$ , were introduced into a three-necked flask equipped with a mechanic stirrer and a dropping funnel. Anisole (0.5 mL, 0.0046 mol) and the solvent (5 mL) were placed in the dropping funnel. Upon dropwise addition of the funnel contents (for ca. 10 min), the reaction was continued at room temperature for 30 min. On completion of the reaction, the catalyst was filtered and washed off with the solvent. The filtrate was shaken with aqueous sodium bicarbonate ( $NaHCO_3$ ), then with water, and finally dried over magnesium sulfate ( $MgSO_4$ ). The selectivity to a particular product was expressed as the amount of this product divided by a total amount of all products, multiplied by 100.

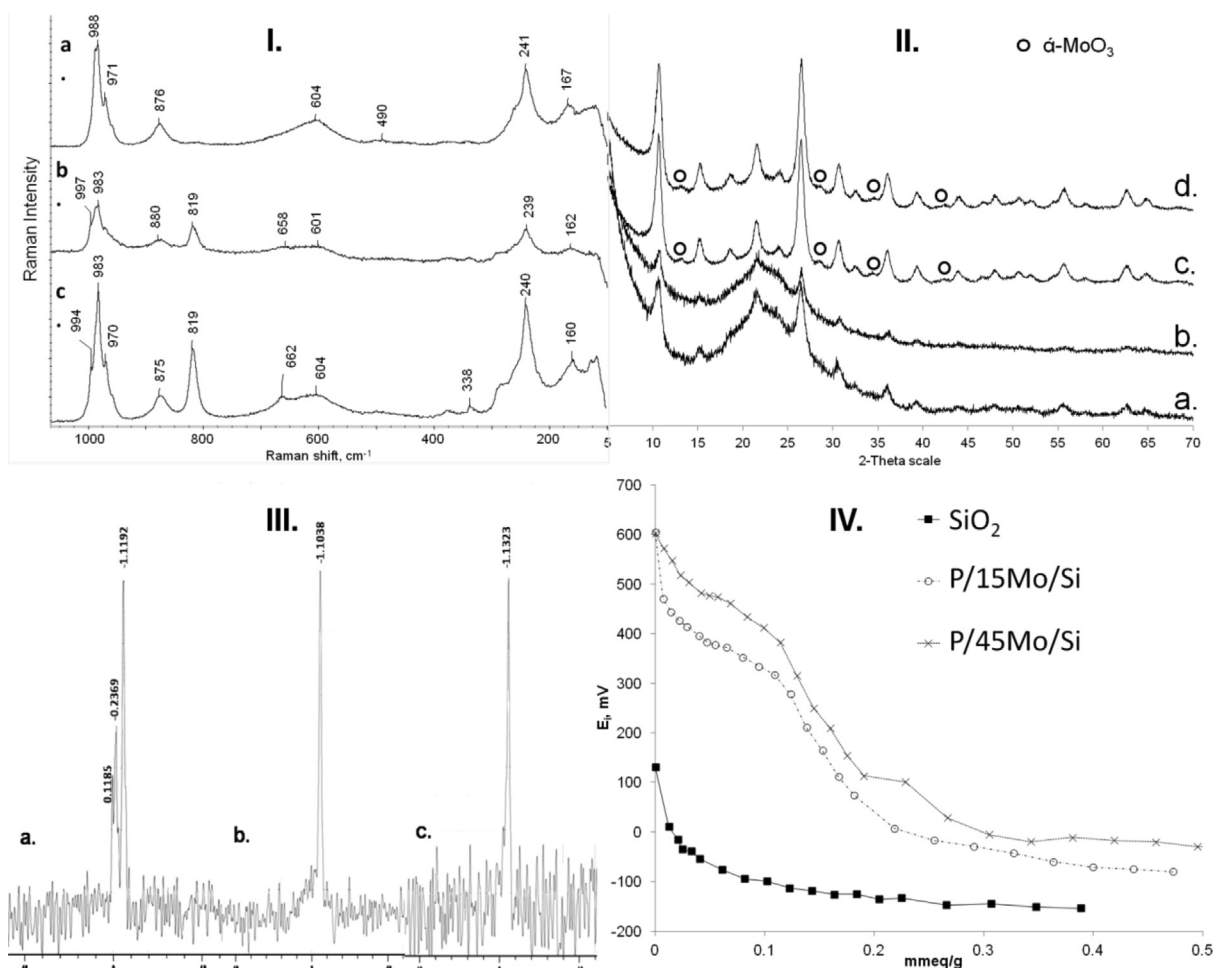
## 3. Results and discussion

### 3.1. Catalysts characterization

To determine the type of the surface domains of the catalysts, Raman (Fig. 1.I), XRD (Fig. 1.II) and  $^{31}P$  MAS NMR (Fig. 1.III) analysis were made.

As a reference for spectral analysis, the solid composed of silica supported phosphomolybdic acid (HPM/Si) was prepared under the same conditions as studied catalysts.

It is postulated that reaction between HPM units and a hydroxylated silica surface occurs and ion pairs with one  $(\equiv SiOH_2)^+$  ( $H_2PMo^-$ ) or more silanol  $(\equiv Si)_m^+ (H_{3-m}PMo)^{m-}$  via simple proton transfer are formed [16]. Due to these reactions, Keggin units undergo slight deformations and the bands for HPM/Si are shifted in comparison to the bands of bulk HPM (996, 980, 900 and  $600\text{ cm}^{-1}$  [17]). Since the spectra for P/Mo/Si are similar to spectra for HPM/Si, HPM formation in P/Mo/Si can be confirmed. Moreover, the bands at 820 and  $994\text{ cm}^{-1}$  indicate the presence of orthorhombic molybdenum oxide ( $\alpha-MoO_3$ ) and it can suggest that  $PO_4$  ions are built in the  $Mo_{\infty}O_{3\infty}$  lattice irregularly. The XRD patterns (Fig. 1.II a and c) show the crystalline nature of the catalysts.



**Fig. 1.** I. Raman spectra of the solids: a. HPM/Si, b. P/15Mo/Si, c. P/45Mo/Si; II. XRD pattern for catalysts: a. P/15Mo/Si, b. P/15Mo/Si after reaction, c. P/45Mo/Si, d. P/45Mo/Si after reaction; III. <sup>31</sup>P NMR spectra of solids: a. HPM/Si, b. P/15Mo/Si, c. P/45Mo/Si; IV. Titration curves for P/15Mo/Si, P/45Mo/Si and SiO<sub>2</sub>.

The main peaks are characteristic for molybdenum hydrogen phosphate. In the pattern for P/15Mo/Si, the peaks for α-MoO<sub>3</sub> are not seen, whereas in the pattern for P/45Mo/Si, they are recognized at 12.7, 28.7, 34.4, 42.1° [18] (together with the peaks for HPM).

Since spectroscopic methods suggest incomplete reaction of phosphates with molybdates, <sup>31</sup>P MAS NMR technique was used to understand the interactions that occur between phosphate, molybdates and silica gel (Fig. 1.III). The multiple signal for HPM/Si probably indicates nearly pure HPM compounds, with different degrees of dissociation on the Si-OH surface. In the spectra of P/15Mo/Si and P/45Mo/Si (Fig. 1.III b and c), the peaks are slightly wider, however, they occur in the same shifts as the main peak for HPM/Si. Thus, it is confirmed that compounds structurally similar to HPM units are formed. It can be suggested that all phosphates are involved in the formation of some heteropolyanions in which PO<sub>4</sub> ions are surrounded with Mo<sub>∞</sub>O<sub>3∞</sub> structures.

The BET surface area analysis (Table 1) demonstrates that the Keggin units in the P/15Mo/Si are more homogeneously dispersed than the composite with higher species loading (P/45Mo/Si). High species loading leads to uneven dispersion of the species or their aggregation across the composites.

The acidity measurements of catalysts samples were carried out by means of potentiometric titration with *n*-butylamine (Fig. 1.IV). The pure silica has only strong acid sites with the initial electrode potential (*E<sub>i</sub>*) of 130 mV (Table 1). Both catalysts have very strong acidic sites. In spite of similar *E<sub>i</sub>* for both P/Mo/Si catalysts, the acidic centers on P/15Mo/Si surface are titrated faster than for P/45Mo/Si.

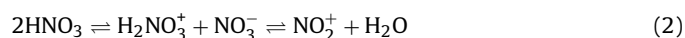
This result suggests higher concentration of strong acidic centers in the P/45Mo/Si than in the P/15Mo/Si.

### 3.2. Anisole nitration

Table 2 lists the results of experiments conducted under similar conditions and P/Mo/Si loading with using fuming and 65% nitric acid. Moreover, for comparison, various anisole nitration results found in the literature are added.

The product analysis showed that only mono- and disubstituted products were formed. There were no traces of the trinitro-derivatives and phenols. As expected, there was no substitution in position 3- to the methoxy group.

The product composition and nitration yield can be explained on the basis of the partial reactions occurred in the reaction medium. When only the fuming nitric acid in the solvent is used, the nitration starts due to the autoprotonation of nitric acid and generation of a nitronium cation NO<sub>2</sub><sup>+</sup>:



As the reaction proceeds, water concentration in the system increases. When it is ca. 8%, the autoprotonation stops and the acid undergoes electrolytic dissociation:



**Table 1**  
Physicochemical characterization of the catalysts.

Catalyst	BET surface area, m <sup>2</sup> g <sup>-1</sup>	Pore volume, cm <sup>3</sup> g <sup>-1</sup>	Pore width, nm	E <sub>i</sub> , mV
SiO <sub>2</sub>	265	0.79	11.4	130
P/15Mo/Si	226	0.64	10.8	605
P/45Mo/Si	124	0.32	10.2	602

**Table 2**  
Anisole nitrations over various nitrating mixtures (NA-nitroanisole, DNA-dinitroanisole).

Nitration system	Anisole conversion, wt.%	Product composition, wt.%			4-/2- Ratio
		2-NA	4-NA	2,4-DNA	
Fuming HNO <sub>3</sub> /C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	54.3	42.6	56.3	–	1.32
65% HNO <sub>3</sub> /C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	6.0	39.5	60.5	–	1.53
P/15Mo/Si/fuming HNO <sub>3</sub> /C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	92.7	37.4	62.2	0.4	1.66
P/15Mo/Si/65% HNO <sub>3</sub> /C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	53.6	34.5	65.5	–	1.90
P/45Mo/Si/fuming HNO <sub>3</sub> /C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	90.5	37.3	59.8	2.9	1.60
P/45Mo/Si/65% HNO <sub>3</sub> /C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	76.4	26.5	73.5	–	2.77
H <sub>2</sub> SO <sub>4</sub> (83.2%)/70% HNO <sub>3</sub> [4]	88.0	36.4	51.9	<0.1	1.43
H <sub>2</sub> SO <sub>4</sub> (86.2%)/70% HNO <sub>3</sub> [4]	87.0	31.8	49.8	5.0	1.57
NO <sub>2</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup> /sulfolane [5]	–	72	27	–	0.38
NO <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup> /CH <sub>3</sub> NO <sub>2</sub> [5]	–	70	29	–	0.41
AcOH/ HNO <sub>3</sub> (3 M) [3]	–	30.5	69.5	–	2.28
NaNO <sub>2</sub> /70% HNO <sub>3</sub> /CCl <sub>4</sub> [6]	–	–	–	–	2.22
Urea(0.5 M)/70% HNO <sub>3</sub> /C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> [6]	–	–	–	–	1.66
H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> 64 mg/1 g of mesoporous SiO <sub>2</sub> /6.9 M HNO <sub>3</sub> [10]	12	18	23	59	1.28
H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> 316 mg/1 g of mesoporous SiO <sub>2</sub> /6.9 M HNO <sub>3</sub> [10]	29	42	50	8	1.19
Acidic montmorillonite clay impregnated with anhydrous Cu(NO <sub>3</sub> ) <sub>2</sub> /Ac <sub>2</sub> O [8]	98	44	52	–	1.18

Then the acid can be easily reduced to HNO<sub>2</sub>:



In excess of HNO<sub>3</sub>, HNO<sub>2</sub> exists essentially as N<sub>2</sub>O<sub>4</sub> [2] but it can also decompose into NO<sub>2</sub>, NO and H<sub>2</sub>O:



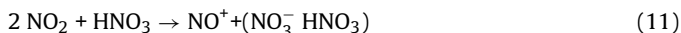
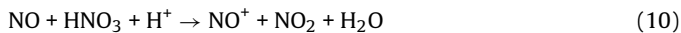
Nitrogen dioxide can also be formed in the reaction of NO with HNO<sub>3</sub>:



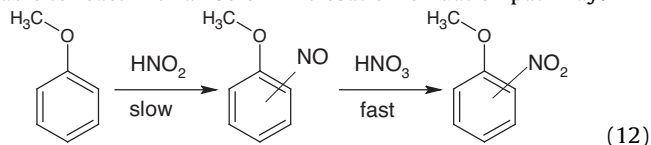
With higher concentrations of HNO<sub>2</sub> and in the presence of water, N<sub>2</sub>O<sub>3</sub> can be formed [2]:



When all these species are present in the reaction medium, NO<sup>+</sup> cations can be formed in the following reactions:



The NO<sup>+</sup> cation is a weaker electrophile than NO<sub>2</sub><sup>+</sup>, however, it is able to react with anisole in nitrosation-oxidation pathway:



Thus, in the beginning of the un-catalyzed reaction with fuming HNO<sub>3</sub>, direct nitration agent is NO<sub>2</sub><sup>+</sup> formed in the autoprotection of HNO<sub>3</sub>. As the nitration reaction proceeds, the concentration of NO<sub>2</sub><sup>+</sup> decreases and NO<sup>+</sup> becomes the main electrophile in the reaction medium, and then nitrosation-oxidation occurs. The nitroso-compounds in the product are not detectable because the kinetics of the nitrosation-oxidation process [2] strongly indicate

that initial C-nitrosation is much slower than oxidation of formed C-nitroso compound.

The used amount of fuming HNO<sub>3</sub> (1:1.5 = anisole:fuming HNO<sub>3</sub>, mole) enables to obtain relatively high anisole conversion to nitroanisoles, i.e. 54.3%. In the more diluted solution of nitric acid (i.e. 65%), the acid undergoes electrolytic dissociation and higher concentrations of HNO<sub>2</sub> and nitric oxides can be present in the reaction medium. As a result, NO<sub>2</sub><sup>+</sup> cation concentration is relatively low and the reaction occurs mainly by nitrosation-oxidation pathway. Under mild conditions with low excess of 65% HNO<sub>3</sub>, only 6% of anisole conversion is obtained.

Selectivity to 4-nitroanisole in the un-catalyzed reactions with both 65% HNO<sub>3</sub> and fuming HNO<sub>3</sub> is similar. The electronic effects of the strongly electron-donating methoxy group are probably responsible for the selectivity. The calculated electron density in the ground state of anisole is the highest around the 2-positions, however, the 4-methoxy substituent can stabilize the arenium ion intermediate [5]. Since in the reaction with 65% HNO<sub>3</sub> the amount of 4-nitroanisole slightly increases, it can be suggested that nitrosation in position 4- in the ring is more favorable than in position 2-. Such selectivity is in agreement with results presented by Thompson and Zeegers [6] that in the presence of NO<sub>2</sub><sup>-</sup>, greater amounts of 4-nitroanisole are obtained (Table 2).

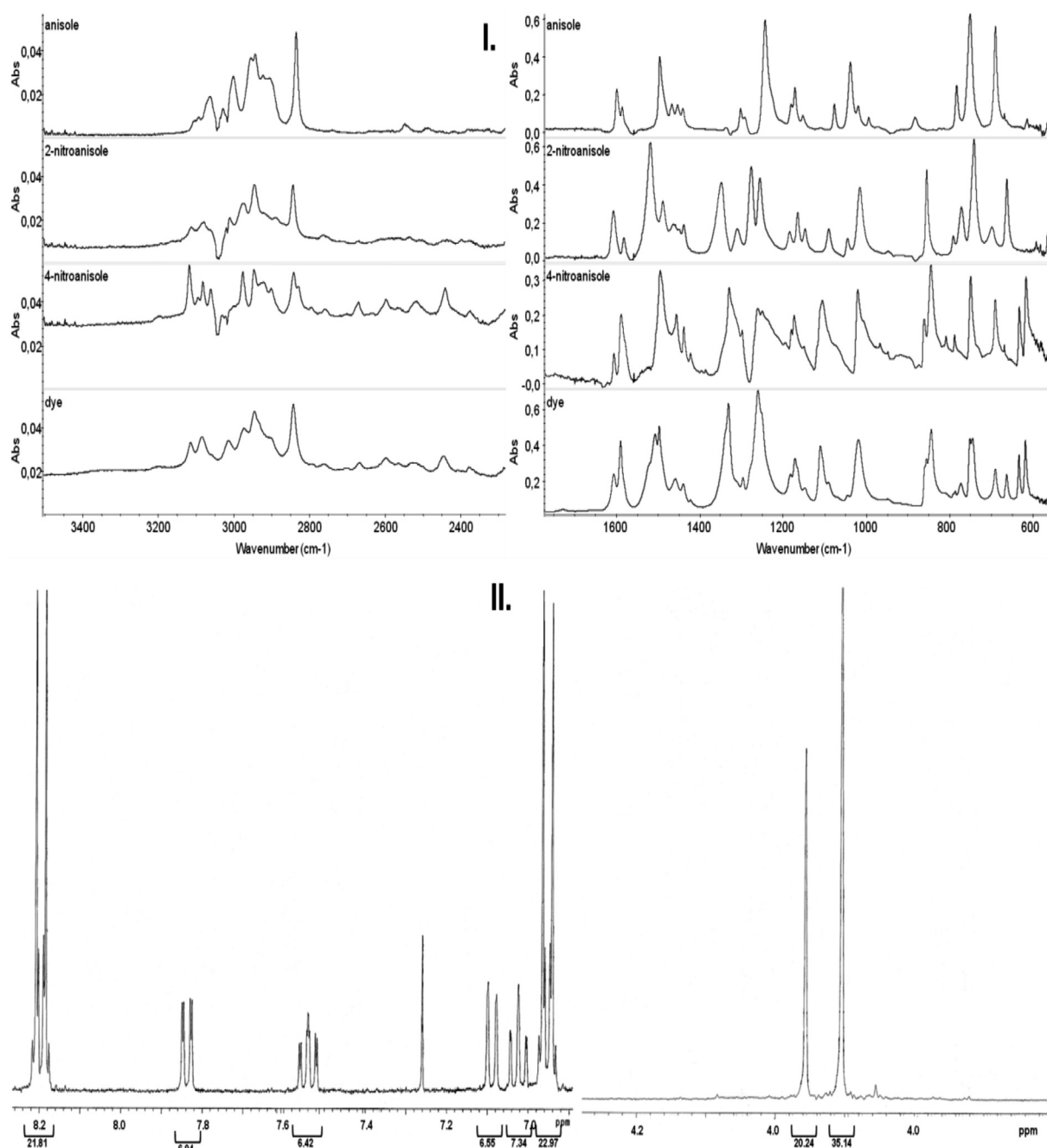
When heterogeneous catalyst is used, the anisole nitration is more effective and the conversion significantly increases in comparison to the un-catalyzed reaction. Due to the presence of strong acid capable of protonating nitric acid, more efficient protonation of fuming HNO<sub>3</sub> occurs, according to the scheme:



Anisole conversion increases to ca. 90% and 2,4-dinitroanisole is observed in the product. Since introducing a second nitro group to the aromatic ring in a one-stage process is possible only with high concentration of NO<sub>2</sub><sup>+</sup> [2], it is likely that in our system the reaction occurs by direct nitration with NO<sub>2</sub><sup>+</sup>. Similar explanation has been given by Barnett et al. [4] for the reactions with 80–90% H<sub>2</sub>SO<sub>4</sub> and 70% HNO<sub>3</sub> (Table 2). Here, we propose that in the P/Mo/Si/fuming HNO<sub>3</sub>/solvent system, concentration of NO<sub>2</sub><sup>+</sup> cation is relatively

**Table 3**  
Re-using of the catalysts.

Nitration system	Anisole conversion, wt.%	Product composition, wt.%			4-/2-Ratio
		2-NA	4-NA	2,4-DNA	
P/15Mo/Si/fuming HNO <sub>3</sub> /C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	90.1	36.3	61.0	2.7	1.68
	90.6	38.0	61.2	0.8	1.61
	90.4	36.6	63.2	0.2	1.73
	90.3	37.3	61.3	1.4	1.64
P/45Mo/Si/65%HNO <sub>3</sub> /C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	76.4	26.5	73.5	–	2.77
	74.5	27.0	72.9	–	2.70
	72.8	26.9	73.1	–	2.72
	72.5	27.1	72.9	–	2.69

**Fig. 2.** I. IR spectrum of the dye and the mixture of anisole and nitroanisoles; II. <sup>1</sup>H NMR spectrum of the dye.



high and, importantly, much higher than in the medium without the catalyst.

For the effective HNO<sub>3</sub> protonation, sufficiently strong acidic sites must be present on the catalyst surface. In the P/Mo/Si catalyst, such acid species are present as (i) protons displaced around heteropolyanions [17] and (ii) protons in the structures of molybdenum oxides (Si-O-Mo(-OH)<sub>2</sub>-O-Si) [19–22]. From the results in Table 2, it is seen that the consumption of anisole is not dependent on the loading of molybdenum-phosphorous species when fuming nitric acid is used. This result can suggest that the concentration of acidic centers in P/15Mo/Si is high enough to obtain high concentration of NO<sub>2</sub><sup>+</sup>. The selectivity in the reaction with fuming HNO<sub>3</sub> is not dependent on the amount of the surface species. In the nitration with 65% HNO<sub>3</sub>, the presence of surface acidic protons facilitates HNO<sub>2</sub> and NO<sup>+</sup> formation from nitric oxides and nitric acid. However, despite of high NO<sup>+</sup> concentration, anisole conversion is lower in comparison to the conversion with fuming nitric acid. Thus, the most effective nitration occurs only when NO<sub>2</sub><sup>+</sup> cations are formed.

On the other hand, when 65% nitric acid is applied the concentration of the surface species is important and in the reaction with P/45Mo/Si/65% HNO<sub>3</sub>/solvent anisole conversion is higher than in the reaction with P/15Mo/Si/65% HNO<sub>3</sub>/solvent. Moreover, in the reaction with P/45Mo/Si/65% HNO<sub>3</sub>/solvent systems, a significant increase in 4-nitroanisole amount is observed in comparison to other systems. Three reasons for higher effectiveness of P/45Mo/Si/65% HNO<sub>3</sub>/solvent system can be proposed:

- (i) Higher concentration of surface HPM, that is the source of electrons, can intensify the reduction of NO<sub>3</sub><sup>-</sup> to HNO<sub>2</sub>. Higher concentration of HNO<sub>2</sub> in the reaction mixture cause the higher amounts of 4-nitroanisole to be formed [6].
- (ii) Slightly higher concentration of the strong acidic sites in P/45Mo/Si can cause more effective NO<sup>+</sup> formation than in the case of P/15Mo/Si.
- (iii) The greater amount of dehydrated surface molybdates in P/45Mo/Si facilitates binding of water formed in the reaction and prevents HNO<sub>3</sub> from the dilution to the concentration below 55% (anisole nitration occurs with HNO<sub>3</sub> concentration of 55% or greater but almost stops below this concentration [6]).

Another issue related to the catalysts performance, is their reuse in consecutive reactions. The catalysts after reactions changed the color from bright greenish to brownish. However, this change does not cause the catalyst activity to be reduced. The re-heated catalysts were re-used in consecutive nitrations and each time they gave similar effectiveness (Table 3). The XRD pattern confirms that after the reaction, similar species are present on the surface (Fig. 1.II. b and d).

Regarding the observed color change, it has been reported previously in the literature that during anisole nitration, the reaction medium has violet-brownish color. Similar behavior of the reaction medium was observed in our research. After separation of the main products by evaporation, the brownish oily residue was obtained. The oil was not volatile and it could not be analyzed by GC/MS, thus the IR spectra were taken (Fig. 2.I). The bands on the recorded spectrum are shifted in comparison to the bands on the spectrum of pure compounds, which suggests that adducts of all nitration products were formed. In the <sup>1</sup>H NMR spectrum of (Fig. 2.II), signals at 3.96 and 3.90 ppm can be assigned to methylene protons from -OCH<sub>3</sub>, whereas signals at 7.0–8.2 ppm can be assigned to protons in the aromatic ring. The ratio of peaks 4:1:1:1:4:3:6 (from 8.2 to

3.9 ppm) suggests the presence of at least three aromatic molecules containing -OCH<sub>3</sub> group. The final structure of the adduct is difficult to recognize, however, the most important is that the dye does not deactivate the solid catalysts and constitutes only ca. 3% of the post-reaction mixture.

#### 4. Conclusions

The anisole nitration is interesting case of aromatic nitration. The presence of -OCH<sub>3</sub> activating group in the ring can suggest that nitration would occur fast and under relatively mild conditions. However, when fuming nitric acid in the organic solvent is used, the reaction does not occur rapidly and only mononitrated anisoles with ca. 50% yield are formed. Thus, it is necessary to use the appropriate nitrating mixture composed of a nitrating agent and an acid catalyst.

It has been presented that silica impregnated with various amounts of molybdenum-phosphorous species is an effective catalyst for nitration of anisole in the presence of fuming or 65% nitric acid under mild conditions. Moreover, by changing concentration of catalysts' surface species it is possible to control the concentration of HNO<sub>2</sub> in the reaction medium. As a result, reaction yield and selectivity to 4-nitroanisoles can be easily controlled. The catalytic systems described in this work can be effectively reused in consecutive reactions.

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