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Short Communication

Interaction of nitromethane with MoO_3/SiO_2 and its influence on toluene nitration

Joanna Adamiak *, Waldemar Tomaszewski, Wincenty Skupiński

Warsaw University of Technology, Faculty of Chemistry, Division of High Energetic Materials, Noakowskiego 3, 00-664 Warsaw, Poland

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ABSTRACT

Interactions of nitromethane with MoO_3/SiO_2 were investigated by infrared spectroscopy. It was found that nitromethane is adsorbed on the catalyst surface and the unique interactions between the molecules and surface species occur. It hinders surface reactions to occur. It is probable that nitromethane hinders diffusion of HNO_3 molecules and NO_2^+ cations to MoO_3/SiO_2 surface and pores in the nitration, but does not hinder diffusion of H^+ and H_2O molecules between solid catalyst phase and solution liquid phase. As a result, the MoO_3/SiO_2/nitromethane system is effective and selective to isomer *ortho*-nitrotoluene.

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1. Introduction

The surface acidic–basic properties of oxides, mixed oxides, or zeolites can be studied using adsorption of probe molecules [1,2]. The use of nitromethane (NM) as the probe molecule has been reported [2]. It was observed that NM can adsorb molecularly, dissociatively, and dissociative–associatively, depending on the basic strength of the sites present on the surface of the studied solids. Nitromethane forms complexes *via* interactions between nitrogen atom (NO_2) or acid hydrogen atoms (CH_3) and oxygen atoms present on the solid surface. These complexes can be determined with infrared spectroscopy (IR) [2].

The zeolites X and Al_2O_3, TiO_2, ZrO_2, and MgO oxides were examined for their abilities to adsorb NM [2]. A shift of IR bands was observed and it depended on the basicity strength of the surface centers. In the solid/NM systems the CH_3 symmetric bending ($\delta_s(CH_3)$ 1404 cm^{-1}) appears at: 1408 cm^{-1} (CsX/NM), 1414 cm^{-1} (LiX/NM) and 1405 cm^{-1} (Al_2O_3/NM). Moreover, NO_2 symmetric stretching band ($\nu_s(NO_2)$) positioned at 1375 cm^{-1} in pure nitromethane shifts to 1378 cm^{-1} (CsX/NM), 1381 cm^{-1} (LiX/NM) and 1379 cm^{-1} (Al_2O_3/NM). The rock angular bending is the most sensitive vibration and it appears at 1100 cm^{-1} in nitromethane IR spectrum and in the range of 1232–1281 cm^{-1} for the examined solids. In the spectra of Al_2O_3, TiO_2, and ZrO_2 a band at 1630 cm^{-1}, related to nitromethane aci-anion is also present.

Molybdenum oxide is an active and selective catalyst. Silica supported molybdenum oxide catalysts (MoO_3/SiO_2) are well-known and have been investigated with respect to their structure and catalytic properties [3–8]. The surface oxygen anions (in the structure of polymolybdates, molybdenum oxides and silica gel) can be potential basic centers that interact with NM.

The surface structures of MoO_3/SiO_2 can participate in the generation of NO_2^+ cation from nitric acid. For that reason MoO_3/SiO_2 has been used as a catalyst in the nitration process. It has been reported that the most active catalyst in toluene nitration is 15% MoO_3/SiO_2 system [9–12]. It is known that NO_2^+ cations can adsorb on the surface oxygen atoms of the catalyst. This process is responsible for a so-called *para effect*, *i.e.* higher selectivity towards isomer *para* in comparison to the non-catalyzed reaction [13,14].

The aim of this work was to investigate the competition between NM and NO_2^+ adsorption on the MoO_3/SiO_2 surface and its influence on the reaction selectivity when the toluene nitration was carried out in NM as a solvent. For stronger adsorption of NM, no *para-effect* was expected to occur. Adsorption of nitromethane on various solid catalysts has been described in the literature [15–18], however no reports on the effect of nitromethane on the catalyst's activity and selectivity can be found. The novelty of our work is that it clearly addresses this issue.

2. Experimental

2.1. Chemicals

Materials: toluene (pure), nitromethane (pure), fuming nitric acid (pure), silica gel (SiO_2), ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$ (pure), magnesium sulfate anhydrous (pure), and sodium hydrogen carbonate (pure). All materials were taken from POCH Gliwice, Poland (except for SiO_2 purchased from Mątwy, Poland and nitromethane purchased from Sigma Aldrich).

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* Corresponding author. Tel./fax: +48 22 2347991.
E-mail address: joanna.adamiak@ichp.pl (J. Adamiak).

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2.2. Methods

Analysis of the reaction products was made using gas chromatography with a Perkin-Elmer Auto System XL and an Rxi-5Sil MS (30 m × 0.53 mm × 1.5 μm) column. The sample of post-reaction mixture was dissolved in nitromethane. The quantitative composition of prepared substances was calculated by internal standard method using peak areas and chlorobenzene as internal standard (IS). Raman spectra were recorded on a Nicolet Almega Dispersive Raman Spectrometer. X-ray powder diffraction patterns were recorded on a Bruker D8 Discover diffractometer. Fourier transform infrared (FT-IR) spectra were recorded using Nicolet 6700 interferometer (4000–400 cm^{-1}, resolution 4 cm^{-1}). Nitromethane was applied on the sample of MoO_3/SiO_2. It was closed in the vessel and after 24 h infrared spectra were recorded.

2.3. MoO_3/SiO_2 preparation

To obtain 5 g of MoO_3/SiO_2 catalyst, 0.9 g (0.75 mmol) of ammonium molybdate tetrahydrate was dissolved in 8 mL of 3% H_2O_2. The solution was applied by wet impregnation method on 4.25 g of SiO_2 (grains 0.6–1 mm). First, the catalyst was dried at 110 °C. Next, it was heated at 300 °C for *ca.* 16 h. As a result, 0.75 g (5.2 mmol) of MoO_3 was obtained (the oxide constituted 15 wt.% of the catalyst mass).

2.4. Nitration process

Toluene or nitromethane (solvent, 10 mL) and 5 g of the catalyst and fuming HNO_3 (0.28 mL, 6.6 mmol) were introduced into a three-necked flask equipped with a mechanic stirrer and a dropping funnel. Toluene (substrate, 4.0 mmol) and solvent (12 mL) were placed in the dropping funnel. Upon dropwise addition of the funnel contents (for *ca.* 10 min) the reaction was continued for 1 h at given temperature. On completion of the reaction the catalyst was filtered and washed off with the solvent. The filtrate was shaken with aqueous sodium bicarbonate, then with water, and finally dried over magnesium sulfate.

3. Results

3.1. Catalyst characterization

To determine the domains obtained on the surface of MoO_3/SiO_2, FT-IR, Raman, and XRD analysis were made.

In the FT-IR spectra (Fig. 1) three main bands at 1100, 800 and 470 cm^{-1} are characteristic for Si – O – Si modes in the silica gel. These broad bands cover the majority of the bands related to molybdenum compounds. However, the bands at 973 cm^{-1} and 567 cm^{-1} may be attributed to polymolybdates and molybdenum oxide in the orthorhombic phase, respectively [3–8].

In the Raman spectra (Fig. 2) the observed bands at 994, 818, 665, 470, 373, 332, 282 and 236 cm^{-1} are characteristic for the orthorhombic molybdenum oxide (α-MoO_3) [3–8]. Weak, broad bands at 946 and 860 cm^{-1} are characteristic for molybdenum ions. The band at 950 cm^{-1} can be assigned to two-dimensional polymeric surface molybdenum species. On the XRD pattern (Fig. 3b) peaks for molybdenum oxide at 2θ angles of 12.8, 23.4, 25.7, 27.3, 33.7, 45.8, 46.3 and 49.3°, and for amorphous silica gel (Fig. 3a) a broad peak at 22° occur.

All these results indicate that domains of crystalline molybdenum oxide and amorphous molybdates are present on the silica support.

Infrared spectroscopy was used to investigate the adsorption of NM on the catalyst surface. Fig. 4 shows the spectrum of pure nitromethane. The nitro group of nitromethane presents two resonance forms that vibrate asymmetrically causing a strong absorption at 1563 cm^{-1} and symmetrically causing a weaker absorption at 1378 cm^{-1} [2]. The bands at 1404 and 1427 cm^{-1} can be assigned to the CH_3 symmetric and asymmetric bending, respectively. The CH_3 rock vibration of NM appears at 1100 cm^{-1}.

In the spectra of the nitromethane-impregnated catalyst (Fig. 4) the following bands are observed: 1562, 1408, 1383 and 657 cm^{-1} (NM), 1100, 800 and 467 cm^{-1} (SiO_2), and 973 and 567 cm^{-1} (MoO_3). Comparing these wavenumbers with those for pure NM, it can be noted that some bands are shifted: the band associated to the symmetric stretching of the nitro group ($\nu_s(NO_2)$) from 1378 to 1383 cm^{-1}, and the band assigned to the CH_3 symmetric bending ($\delta_a(CH_3)$) from 1404 to 1408 cm^{-1}. The characteristic band for NM at 1100 cm^{-1} is covered by a broad band assigned to silica gel. The characteristic bands for nitromethane aci-anion (1628, 1539, 1489, 1371, 1282, 1180 cm^{-1} [2]) are not observed. The wavenumber shifts confirm that NM is indeed adsorbed on the MoO_3/SiO_2 surface. Moreover, it indicates that the basic centers are present on the catalyst surface.

A smaller shift in the wavenumber of CH_3 bending vibration (from 1404 to 1408 cm^{-1}) in comparison to the shift in the wavenumber of NO_2 symmetric stretching vibration (from 1375 to 1383 cm^{-1}) suggests that the interactions between the NO_2 group and the surface are stronger than the interactions between the CH_3 group and the surface. This was not the case for zeolites where greater shifts for CH_3 bending and rock angular bending bands were reported [2].

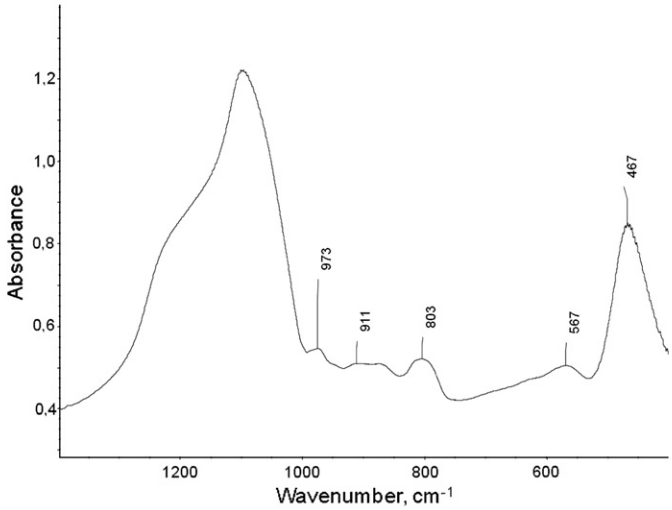

Fig. 1. Infrared spectrum of MoO_3/SiO_2.

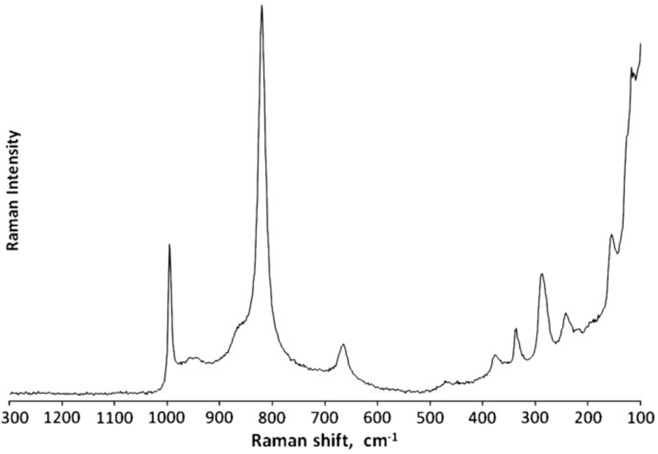

Fig. 2. Raman spectrum of MoO_3/SiO_2.

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