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Mo/ZSM-5 Catalysts for Methane Aromatization. Study of the Mo Precursor Species in Impregnation Solution of Ammonium Heptamolybdate

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Abstract

A change in the ratio between monomeric and polymeric molybdenum species regarding the concentration and pH of the impregnation solutions will probably make a significant effect on the nature and number of active sites of Mo/ZSM-5 catalysts. To provide the control of molybdenum species in solutions, we have studied the dependence of structure of molybdenum species in the initial impregnation solutions of ammonium heptamolybdate on the concentration and pH of these solutions (from electron absorption spectra). When the concentration of solutions is low or pH increases, there are no polymeric molybdenum species. Besides, there is a region where monomeric and polymeric species exist at a time. At higher concentrations or when pH decreases, monomeric species transform almost completely into polymeric species.

INTRODUCTION

Mo/ZSM-5 catalysts are the most promising for dehydro-aromatization of methane to benzene. It was reported that a methane conversion of 4–8 % could be achieved at benzene selectivity of 70–90 % [1–4]. The recent attention has been paid to the suppression of carbonaceous deposit formed during the methane aromatization over Mo/ZSM-5 catalysts [5].

Mo/ZSM-5 catalysts are traditionally prepared by impregnating a zeolite with an ammonium heptamolybdate solution ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) [1–5]. The introduction of other metals by impregnation (Ru) or ion exchange (Cu) into zeolites permits a significant improvement of the catalytic performance [6, 7]. However, the difference of conditions of impregnation (concentration and pH of solutions, temperature and duration of impregnation) and following thermal treatment stages (temperature, duration and medium composition) as well as a Si/Al ratio and a form of the initial zeolite hinder a comparison of the reference data and a choice of the optimal preparation method and composition of Mo/ZSM-5 catalysts.

The information on the Mo species and its localization in the zeolite structure is quite contradictory. Thus, many kinds of active site in the catalyst and the reaction mechanism have been proposed. In most publications, emphasis is given to the role of molybdenum carbide, formed in the catalyst during the induction period. It is indicated that Mo_2C are the active sites responsible for the methane activation to produce ethane or ethylene [5, 8, 9]. The role of states Mo^{4+} and Mo^{5+}, observed in the zeolite along with molybdenum carbide, is still unclear [8]. Localization of the reaction active sites is the other controversial subject.

In recent publications emphasis has been placed on the role of carbonaceous deposits formed during the methane dehydro-aromatization. It is commonly accepted that carbonaceous deposits on the catalyst surface is the main reason of their deactivation [5, 10]. However, carbonaceous deposits play a positive role at the initial stage of reaction, because coke modification of the Mo_2C surface decreases its reactivity in the side reaction of methane decomposition to hydrogen and carbon [8, 11]. Some researchers suggest that coke formation on the Broensted acid sites of zeolites can also result in the catalyst deactivation [10, 11].

Therefore, Mo/ZSM-5 catalysts may be of interest for studying the possibility to increase their stability to coke formation during the reaction. To solve the problem, one should provide a systematic study of Mo/ZSM-5 properties regarding the conditions of their synthesis. In addition, it is of prime importance to have a clear idea of the species of molybdenum even in the initial ammonium heptamolybdate solutions. This is determined by the ability of molybdenum to form both monomeric and polymeric species in solutions [12, 13]. It is possible that a change in the ratio between these species regarding the concentration and pH of impregnation solutions can significantly affect the nature and number of active sites in future catalysts.

The aim of this work was to gain information concerning the species of molybdenum in ammonium heptamolybdate solutions.

METHODS

Solutions of molybdenum (2 10^{-6}–10^{-1}M) were prepared from ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. To vary pH values of solutions, we added either hydrochloric acid or ammonia solutions. Hydrochloric acid has no absorption bands in the region of heptamolybdate absorbance in comparison with other acids *e. g.* nitric or sulfuric acids. An EV-74 universal ionomer was used to measure pH of ammonium heptamolybdate solutions.

Electron spectra of ammonium heptamolybdate solutions were recorded with a UV-VIS spectrophotometer (Specord M40) at a wave length of 200–500 nm.

RESULTS AND DISCUSSION

As the molybdenum concentration increases from 2 10^{-6} to (2–5) 10^{-4}M, pH of solutions decreases from ~6.2 to ~4.4. When the concentration increases from (2–5) 10^{-4} to 10^{-1}M, pH increases from ~4.4 to ~5.5.

According to reference data [12, 13], molybdenum forms monomeric species in very dilute solutions of ammonium heptamolybdate (the concentration of molybdenum is lower than 10^{-4} M) irrespective of pH values. The equilibrium between different molybdenum species is described by below equations:

$$MoO_4^{2-} + H_2O = HMoO_4^- + OH^- \qquad (1)$$

$$HMoO_4^- + H_2O = H_2MoO_4 + OH^- \qquad (2)$$

In this case, $HMoO_4^-$ and H_2MoO_4 species predominate in the solution at pH<4 [12]. In our solutions (the molybdenum concentration is lower than (2–5) 10^{-4} M and pH > 4.4), molybdate ion MoO_4^{2-} is the predominant species. The value of pH is likely determined by equation: $NH_4^+ + H_2O = NH_4OH + H^+$. A decrease in the concentration of ammonium heptamolybdate in the above region shifts the equilibrium to the left, that is pH of the solution increases.

For more concentrated ammonium heptamolybdate solutions (the concentration of molybdenum is higher than 10^{-4}M), the equilibrium between different molybdenum species is described by below equations [12]:

$$7\,MoO_4^{2-} + 4H_2O = Mo_7O_{24}^{6-} + 8OH^-, \quad 4.5 < pH < 5.5 \qquad (3)$$

$$7\,MoO_4^{2-} + 5H_2O = Mo_7O_{23}(OH)^{5-} + 9OH^-, \quad 3.5 < pH < 4.5 \qquad (4)$$

$$7\,MoO_4^{2-} + 6H_2O = Mo_7O_{22}(OH)_2^{4-} + 10OH^-, \quad 2.5 < pH < 3.5 \qquad (5)$$

$$7\,MoO_4^{2-} + 6H_2O = Mo_7O_{21}(OH)_3^{3-} + 11OH^-, \quad pH < 2.5 \qquad (6)$$

$$19\,MoO_4^{2-} + 17H_2O = Mo_{29}O_{59}^{4-} + 34OH^-, \quad pH < 2.0 \qquad (7)$$

Consequently, when the molybdenum concentration in studied solutions is higher than (2–5) 10^{-4} M and pH>4.4, the equilibrium between molybdenum species co-existing in the solution can be described by equations (3) and (4). The fact that pH increases with increasing molybdenum concentration can be attributed to an increase in the degree of molybdenum polymerization.

It was interesting to use electron spectroscopy for studying the solutions of ammonium heptamolybdate in order to provide fast control of molybdenum species in solutions in future.

On varying the molybdenum concentration from $2\ 10^{-6}$ to $2.5\ 10^{-4}$M, the electron absorption spectra of ammonium heptamolybdate solutions contain a broad absorption band, which probably results from a superposition of two bands with closely situated maximums. Thus, in the short-wave spectrum part, one can distinguish a maximum of the first absorption band which corresponds to a wave length of ~208 nm. The maximum of the second band is less pronounced (227 nm). According to [14, 15], both bands are attributable to absorption of a molybdate ion. When the concentration rises within the above range, the degree of absorption increases and the band shifts to the long-wave spectrum part. Note that the maximum at ~208 nm does not practically shift.

When the molybdenum concentration exceeds $2.5\ 10^{-4}$M, the spectrum does not contain pronounced absorption bands. In addition, the absorption edge also shifts to more long waves if the concentration of molybdenum increases. According to [16], this shift may suggest an increase in the degree of molybdenum polymerization.

Figure 1 presents typical electron absorption spectra of ammonium heptamolybdate solutions with different concentrations.

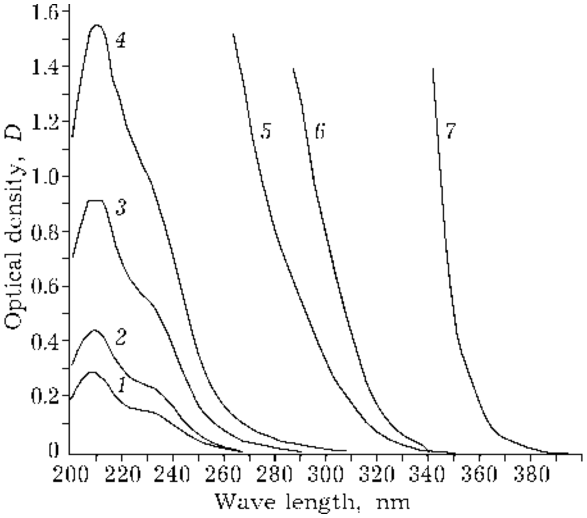

Fig. 1. Electron absorption spectra *vs.* concentration (*C*) of ammonium heptamolybdate solutions. *C*, M: $2.5\ 10^{-5}$ (*1*), $5\ 10^{-5}$ (*2*), $1\ 10^{-4}$ (*3*), $2\ 10^{-4}$ (*4*), $1\ 10^{-3}$ (*5*), $2\ 10^{-3}$ (*6*), 0.1 (*7*).

Using the Buger – Lambert – Beer law ($\varepsilon = D/(c\ l)$, where D is optical density, c – molar molybdenum concentration, and l – length of absorbing layer) to calculate the molar extinction coefficient for solutions with different concentrations at a fixed value of wave length, we have shown that the law is obeyed for two concentration ranges: $2\ 10^{-6}$–$5\ 10^{-5}$ and $2\ 10^{-3}$–10^{-1} M. Each concentration range is characterized by similar light-absorbing molybdenum species: monomeric molybdate ions for $2\ 10^{-6}$–$5\ 10^{-5}$ M and polymeric molybdenum species for $2\ 10^{-3}$–10^{-1} M. When the molybdenum concentration ranges from $5\ 10^{-5}$ to $2\ 10^{-3}$ M, the Buger–Lambert–Beer law is not confirmed, which indicates that the molybdenum species are not homogeneous and they amount is different.

Alkalizing of strongly diluted solutions of ammonium heptamolybdate (the molybdenum concentration is $2\ 10^{-5}$ M, $\mathrm{pH}_{\mathrm{initial}}$ 5.5) to pH~10 does not result in changes in electron spectra, which indicates that the species of molybdenum in the solution remains unchanged. Taking into account eqs. (1) and (2), describing the equilibrium in such diluted molybdenum solutions, one can suggest that molybdenum presents as a molybdate ion in the above solution. The fact that the Buger–Lambert–Beer law is applicable for the solutions with lower concentrations, $2\ 10^{-6}$–$5\ 10^{-5}$M at $\mathrm{pH}_{\mathrm{initial}} > 5.5$ permits a suggestion that molybdenum exists in such solutions as a molybdate ion only.

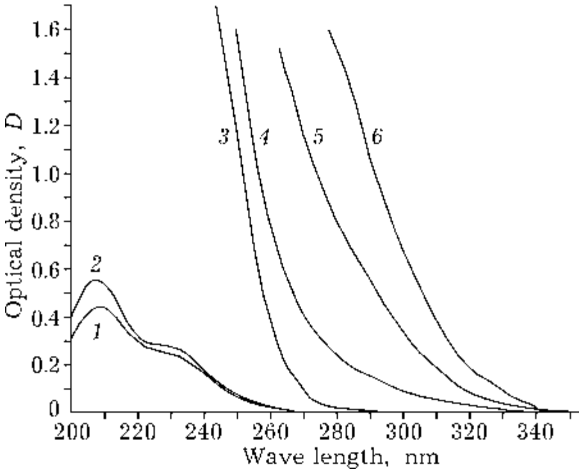

Fig. 2. Electron absorption spectra *vs.* pH of ammonium heptamolybdate solutions. *C*, M: $5\ 10^{-5}$ (*1, 2*), $1\ 10^{-3}$ (*3*–*6*); pH: 5.3 (initial) (*1*), 6.9–8.3 (*2*),6.5–8.0 (*3*). 4.9 (*4*), 4.5 (initial) (*5*), 3.0 (*6*).

For 5 10^{-5} M molybdenum solutions ($pH_{initial}$ 5.3), an increase of pH to 6.9 provides a small increase in the absorption degree (Fig. 2). As pH increases to 8.3, electron spectra not change. This increase in pH causes a leftward shift of the equilibrium, described by eq. (1), resulting in a molybdate ion concentration increase.

When the concentration of molybdenum is >2 10^{-4} M, alkalizing of ammonium heptamolybdate solutions involves a shift of the initial absorption edge to the short-wave spectrum part. According to reference data [16], changes in the spectra indicate a transition of polymeric molybdenum species into a monomeric species as a molybdate ion. In every case pH reaches some limiting value above which the electron spectra remain unchanged. For instance, for concentration 1 10^{-3}M the limiting value of pH is 6.5 (see Fig. 2). This fact suggests that molybdenum has completely transformed into a monomeric species.

By contrast, acidifying of ammonium heptamolybdate solutions with a molybdenum concentration ranging from 2 10^{-4} to 10^{-1} M results in a shift of the initial absorption edge to a long-wave spectrum part. In this case, changes in the spectrum show an increase in the polymerization degree according to eqs. (3)–(7).

Figure 2 shows electron spectra of ammonium heptamolybdate solutions (the molybdenum concentration is 1 10^{-3} M and $pH_{initial}$ 4.5) to illustrate their dependence on pH variations.

Thus, electron spectra of absorption of ammonium heptamolybdate solutions permit one to follow changes in the molybdenum species when the concentration and pH of solutions are varied.

Calculations of the molar extinction coefficient of ammonium heptamolybdate solutions of different concentrations at the fixed value of pH and the specified wave length (Fig. 3, *a*) show that the coefficient does not practically change within a broad range of molybdenum concentration, 2 10^{-5}–10^{-1} M, at pH > 7, which indicates that molybdenum presents in the same species in the considered solutions. Since molybdenum exists as a molybdate ion (MoO_4^{2-}) in a 2 10^{-5} M solution, this monomeric species characteristic of strongly dilute solutions of ammonium heptamolybdate maintains at higher molybdenum concentrations at pH > 7.

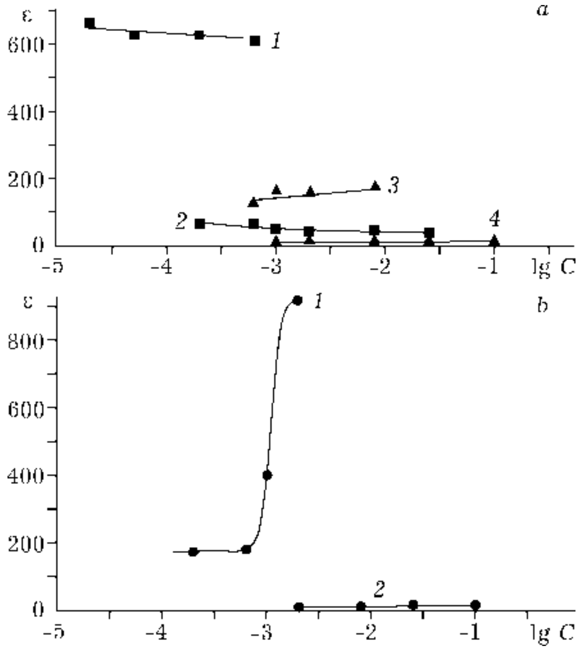

Fig. 3. Dependence of molar extinction coefficient (ε) on concentration of molybdenum (*C*) when pH and wave length (λ) are fixed: *a* – λ = 256 (*1*), 274 (*2*), 322 (*3*) and 357 nm (*4*); pH 7.0 (*1, 2*) and 2.5 (*3, 4*); *b* – λ = 278 (*1*) and 345 nm (*2*); pH 4.7.

When the value of pH is fixed at 2–4, the dependence of the molar extinction coefficient on the molybdenum concentration in the above solutions (6 10^{-4}–10^{-1} M) changes also insignificantly (see Fig. 3, *a*). As previously noted, acidifying of molybdenum solutions at the above concentration range results in the increase in the degree of molybdenum polymerization and in predomination of the polymeric molybdenum species in the solutions. In addition, the fact that the molar extinction coefficient for the above solutions is constant may indicate that the ratio of different polymeric molybdenum species is equal or they are similar.

As follows from Fig. 3, *b*, the molar extinction coefficient is not constant when molybdenum concentration is varied and pH is fixed at 4–6.

Thus, the present data indicate that polymerization does not occur upon low molybdenum concentration or increasing pH of solutions. But there is another region where polymeric and monomeric molybdenum species exist at a time. Monomeric species almost completely transform into polymeric species at higher concentrations of molybdenum and as pH of solutions decreases. We suggest that the species of molybdenum in the solution can affect the state of the active component in Mo/ZSM-5 catalysts prepared from solutions of ammonium heptamolybdate as in the case of Mo/Al_2O_3 catalysts [17].

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