Impregnation of Catalytic Active Components in an Ammonia Solution During Granulation of Aluminium Hydroxide Gel by Sol-Gel Method in Hydrocarbon-Ammonia Moulding Column

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In this paper the impregnation of the catalytic active components during granulation of the Al(OH)₃ gel using the hydrocarbon-ammonia moulding (HAM) is studied. It is identified that the granulation of the spherical Al(OH)₃ gel in ammonia medium in which are previously dissolved the active components (AC) is better method. During the granulation in the ammonia aqueous solution the aluminium hydroxide gel do not selectively adsorb the catalytic active component and the AC are in the concentration equilibrium between the ammonia aqueous solution and water holded in the network structure of the spherical gel. A content of the AC in the catalyst produced (treated thermally) is quantitatively related to their concentrations in ammonia aqueous solution. The catalysts for the hydrodesulfurization prepared by the impregnation of the AC during the granulation of the Al(OH)₃ gel in the ammonia medium by using the HAM method have better activities and mechanical strength in comparison with a commercial catalyst prepared by pore volume impregnation.

Keywords: hydrocarbon-ammonia moulding, granulation of the Al(OH)₃ gel, hydrodesulfurization, pore volume impregnation, γ-alumina

Catalysts which are used commercially and widely for petroleum refining hydrosulfurization (HDS) and hydrodenitrogenation (HDN) are based on sulfide transition metals such as Ni or Co and Mo or W. γ-Alumina is typically used as a support for these catalytic active components due to its good mechanical and textural properties. γ-Alumina has an ability to provide high dispersion of the catalytic active components and thus it is most widely used as the support for metals, metal oxides, metal sulfides or their mixtures in chemical industry. It is known that there are various methods for supporting the active components (AC), such as co-precipitation, mixture, impregnation, ion exchange methods and so on. Generally, the γ-alumina supported catalysts have an irregular distribution of the AC and inequable bonding conditions between the AC and support due to selective local adsorption of the transition metal oxides from precursors in the catalyst preparation stage. Hence, the catalysts produced by above-mentioned their methods have some drawbacks for characterizations and performances, such as lower activity, selectivity, mechanical strength, thermal stability and so on. It is industrially recognized that pseudo-boehmite aluminium hydroxide is synthesized by using not only a periodic precipitation from the solutions of sodium aluminate with acids or from the solutions of aluminium salts (nitrates, sulfates) with alkali [1], but also continuous precipitation method. Spherical granules of γ-alumina are generally prepared via the following stages: preparation of aluminium hydroxide gel from the precursors, formation of pseudosol from the prepared gel by peptizer acid, sphere-forming of aluminium hydroxide gel, washing filtration, drying and calcination. Methods which are most widely used to produce spherical granules are rotating pan granulation, gas phase granulation, liquid phase moulding, oil moulding and hydrocarbon-ammonia moulding (HAM) [2]. In our study the HAM method is used. We have investigated preparation method of the catalyst supported on the spherical alumina, with high activity, high mechanical strength and uniform size, by the impregnation of the AC during the formation of spherical alumina from pseudosol Al(OH)₃ in kerosene-ammonia layer (catalytic active components have been previously dissolved in ammonia), using the HAM.

Experimental part

The aluminium hydroxide gel is prepared by a simultaneous dropping method from the solutions of sodium aluminate and nitric acid at 20-25 or 90-100°C. The solution of sodium aluminate, with a molar ratio Na₂O/Al₂O₃ 1.8-2.0 and a concentration of aluminium oxide in the solution 90-110 g·Al₂O₃/ℓ, and the solution of nitric acid with a percentage concentration 20-25 wt.% have been used in our experiments. The aluminium hydroxide gel prepared have different properties depending on the precipitation conditions (precipitation temperature, pH and temperature of precipitate aging and so on). Regarding the precipitation temperature, the precipitate obtained is distinguished as so-called “cold” (< 25°C) or “hot” (90-100°C) one. In the case of both the cold and hot precipitates, the precipitation was carried out for 1-1.5 h and with stirring rate 40-60 rpm. Especially, in the case of the cold precipitation, one was carried out at pH 8.5-9, then the precipitate was homogenized for 1 h and was aged for 1 h at temperature > 90°C, while in the case of the hot one, the precipitate was only homogenized at pH 8-8.5. If pH was lowered during the precipitate homogenization and aging, the sodium aluminate is added in order to keep it up. After the aging the hydroxides of the cold and hot precipitation are mixed in definitive ratio to provide better filtering and washing.
We have controlled the porous structure of the activated alumina, with a mixing ratio of the cold precipitate to the hot one. For the alumina with the micropores we have used the mixing ratio 3:7-5:5 (cold:hot) while in the opposite case the ratio 5:5-7:3.

Pseudosol Al(OH)_3, (plastic sol) is prepared by using the nitric acid as a peptizer and at this time an amount of HNO_3 added was molar ratio HNO_3/Al_2O_3 of 0.15-0.2 independent of the precipitation conditions.

After the pseudosol Al(OH)_3 preparation, a granulation (sphere-forming) of the aluminium hydroxide gel was carried out using the hydrocarbon-ammonia moulding (HAM). A kerosene was used for the HAM. Figure 1 shows an experimental apparatus for the preparation of spherical alumina from pseudosol Al(OH)_3.

The pseudosol Al(OH)_3, obtained by treating the pseudoboehmite aluminium hydroxide by an acid-peptizer drops through a die plate in bottom of a pseudosol container into the kerosene layer on top of the moulding column. There the plastic sol takes spherical shape due to the surface tension. Thereafter, sol spherical granules are transformed in to gel in the coagulant medium and thus they are congealed, falling down into the ammonia solution. Further on, the gel spherical granules are thermally treated to produce spherical alumina, dried at 90-100°C and calcined at 600°C.

The ammonium dichromate and heptamolybdate, nitrate of Ni, Cu, Co and so on are used to impregnate the catalytic AC such as Ni, Co, Mo, Cr, Cu and so on over a support during the granulation of the aluminium hydroxide gel. The chemical compounds with required metals have been previously dissolved in the ammonia medium before the granulation.

For identification of a performance of the catalyst produced using the impregnation of the AC over the support during the granulation of the aluminium hydroxide gel, we have prepared hydrotreating catalysts, Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3. The composition of the AC in the catalysts investigated was CoO (or NiO) 4 wt. %, MoO_3 12.5-13 wt. %. The HDS activities were tested in a high pressure flow micro-reactor system. The micro-reactor system was operated at 350°C, 3.8MPa and LHSV=4 h⁻¹. For comparison, α-alumina supported Co-Mo catalyst was also tested under the same conditions. The commercial catalyst compared also had the same compositions mentioned above. Prior to the HDS test, the catalysts were sulfided at 350°C and 2MPa of H₂ for 8 h. A mixture of 4 mol. % CS₂ in cyclohexane is used for the sulfidation of three catalysts investigated. We measured the total sulfur content of the liquid product, using combustion/fluorescence technique following ASTM 5463 method in an Antek 9000 NS analyzer.

Results and discussions

The impregnation of the catalytic AC into the spherical aluminium hydroxide gel during the granulation can follow such four methods as are presented in figure 2.

To analyze the utilization possibility, merits and demerits of the methods presented in figure 2, we observed an influence of the impregnation methods of the AC on stability of the pseudosol Al(OH)_3 during the granulation and described observation results in table 1. In the impregnation methods, an amount of the chemical compound (with the active component) added into the ammonia aqueous solution was 4 wt. % (converted into the oxide) and a molar ratio of acid-peptizer to Al_2O_3 was 0.14 mol/mol.

It is evaluated the impregnation methods of the AC during the granulation from table 1 and figure 2. Using the methods (a) and (b), a part of the nitric acid reacts with the AC added into the ammonia transforming into a nitrate. The formed nitrate decreases the stability of the pseudosol because itself acts as the coagulant of the sol. Therefore, in the case of the co-precipitation of the pseudoboehmite aluminium hydroxide with the active component, Ni(OH)_2, Co(OH)_2, Cu(OH)_2 and so on are not quantitatively precipitated with Al(OH)_3. This means that it is difficult to obtain the catalysts with required content of the AC. Thus, one can know that the co-precipitation method is ideal in case that two components precipitated are chemically combined like a aluminosilicate-catalytic cracking catalyst and two methods ((a) and (b)) mentioned above have essential demerits.

From a view of the control of content of the active component in the catalyst, the method (c) is more reasonable than methods (a) and (b). In this case of the method (c), the catalytic AC mixed with Al(OH)_3, have not influence on the stability of the pseudosol, since they are not well dissolved in pseudosol acidified due to peptization by the acid, but they can be eluted into the ammonia medium from gel after the granulation. To analyze this elution problem, we observed a relation between a
residence time of the spherical aluminium hydroxide gel in the ammonia medium and a elution of the catalytic AC (fig. 3). From figure 3 one can find that relatively more Mo and W are eluted, and then Ni and Co occupy second order for the elution and a little of V and copper chromite are eluted. This fact is related to solubility order of the AC in the ammonia aqueous solution. Thus the method (c) is also not good.

Then the method (d) is selected for the granulation. For this method the catalytic AC also has no influence on the stability of the pseudosol Al(OH)₃ since they were not added to it. In addition, the precursors of such catalytic AC as Ni, Co, Mo, Cu, Cr, and etc. used widely as catalysts in the petroleum refining and chemical industry are well dissolved in the ammonia aqueous solution. For the method (d) it is important to analyze the quantitative relation between a concentration of the AC in the ammonia medium and their contents in the catalysts obtained. In other words, it should be precisely analyzed that ions or molecules of the catalytic AC are selectively adsorbed onto the local inner surface of the spherical gel or they are in a concentration equilibrium between the ammonia medium and water holded in network structure of the hydrated gel. In reference to the hydrated gel, note that it consists of the network structure arrangement of the Al(OH)₃ particles, in which water is holded. To this analysis, we observed a dependence of the content of the AC in the catalyst produced on the residence time of the spherical aluminium hydroxide gel and their concentrations in the ammonia medium. In order to observe the relation between the amount of the catalytic AC in the ammonia aqueous solution and the content of the AC in the hydrated alumina gel, we took out the active component impregnated hydrated gel from the HAM column at 10 min intervals and after the thermal treatments (drying and calcining(600°C)) we measured the content of the active component. Figure 4 reveals the relation between the residence time of the spherical gel with different mixing ratio of the cold to hot precipitates in the HAM column and the content of the AC in the catalyst produced in the case of the concentration of the active component 3.5 wt. % in ammonia medium, while figure 5 shows that in the case of 1 wt. %.

The several characteristics of the spherical Al(OH)₃ gel with different mixing ratio (cold:hot) are described in table 2. From figure 4 and 5 one can see that in both cases the impregnation of the AC reached the equilibrium at the residence time 40-50 min and the more cold precipitate the spherical gel contains, the more quick concentration equilibrium is reached. Diameters of the spherical aluminium hydroxide gel measured were in 5.0-5.5mm intervals. It is due to the fact that the more cold precipitate the pseudosol Al(OH)₃ includes, the more water is holded in it and thus in the hydrated gel state the diameter of its network is large, so that a diffusion of the ions is more easy.

**Table 1**

<table>
<thead>
<tr>
<th>No.</th>
<th>Active component</th>
<th>Compounds with active components</th>
<th>Impregnation method used</th>
<th>Stability of pseudosol</th>
<th>Thixotropic property</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuO</td>
<td>Co(OH)₂</td>
<td>(a) or (b)</td>
<td>Be not peptized</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>NiO</td>
<td>Ni(OH)₂</td>
<td>(a) or (b)</td>
<td>Be not peptized</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>CuO</td>
<td>Cu(OH)₂</td>
<td>(a) or (b)</td>
<td>Be not peptized</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>CoO</td>
<td>Co(OH)₂</td>
<td>(c)</td>
<td>Concentration after a certain time</td>
<td>Loss</td>
</tr>
<tr>
<td>5</td>
<td>NiO</td>
<td>Ni(OH)₂</td>
<td>(c)</td>
<td>Concentration time delay</td>
<td>Loss</td>
</tr>
<tr>
<td>6</td>
<td>CuO</td>
<td>Cu(OH)₂</td>
<td>(c)</td>
<td>A little decrease of稳定性</td>
<td>Conservation</td>
</tr>
<tr>
<td>7</td>
<td>WO₃</td>
<td>H₂WO₄</td>
<td>(c)</td>
<td>A little decrease of stability</td>
<td>Conservation</td>
</tr>
<tr>
<td>8</td>
<td>V₂O₅</td>
<td>V₂O₅</td>
<td>(c)</td>
<td>A little decrease of stability</td>
<td>Conservation</td>
</tr>
<tr>
<td>9</td>
<td>MoO₃</td>
<td>H₂MoO₄</td>
<td>(c)</td>
<td>A little decrease of stability</td>
<td>Conservation</td>
</tr>
</tbody>
</table>

Fig. 3. Dependence of elution of the active components on residence time of Al(OH)₃ gel in ammonia aqueous solution with concentration 10 wt. %. The initial content of active components in the Al(OH)₃ gel is 4.5 wt. %. 1 - Co(OH)₂; 2 - Ni(OH)₂; 3 - H₂WO₄; 4 - H₂MoO₄; 5 - V₂O₅; 6 - copper chromite (Cu₂Cr₂O₇).

Fig. 4. Content of active component in the catalyst produced as a function of residence time of spherical Al(OH)₃ gel (diameters 5 - 5.5 mm) in ammonia aqueous solution at concentration of active component in ammonia 3.5 wt. %. Mixing ratio of cold to hot precipitates: 1 - 3:7, 2 - 5:5, 3 - 7:3. • NiO; Δ Cr₂O₇; MoO₃.
Fig. 5. Content of active component in the catalyst produced as a function of residence time of spherical Al(OH)₃ gel (diameters 5 ~ 5.5 mm) in ammonia aqueous solution at concentration of active component in ammonia 1.0 wt. %. Mixing ratio of cold to hot precipitates: 1 - 3:7; 2 - 7:3. NiO; CrO₃; MoO₃

Table 2
CHARACTERISTICS OF THE SPHERICAL Al(OH)₃ GEL

<table>
<thead>
<tr>
<th>Mixing ratio (cold:hot)</th>
<th>Content of the water in the spherical gel, wt.%</th>
<th>Ignition loss of the dry gel, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:7</td>
<td>72</td>
<td>15</td>
</tr>
<tr>
<td>5:5</td>
<td>77</td>
<td>15</td>
</tr>
<tr>
<td>7:3</td>
<td>80</td>
<td>15</td>
</tr>
</tbody>
</table>

Our experimental results are consistent with the ones of a reference [3] in which was observed that selective adsorption of the catalytic AC did not occur at pH of impregnated solution 9 for the impregnation of NiO, CoO and MoO₃ onto activated alumina.

Based on the observation mentioned above, we have prepared the catalysts for the HDS and HDN, Co-Mo/γ-alumina and Ni-Mo/γ-alumina, using the granulation method in ammonia medium in which are previously dissolved the active components (fig. 2 (d)) and made a comparison between the HDS activity of the catalysts prepared by us and one of a commercial catalyst extruded. The latter was prepared by pore volume impregnation using aqueous solutions of (NH₄)₂Mo₇O₂₄ · 24H₂O and Co(NO₃)₂ · 6H₂O. The several physical properties of the catalysts investigated are shown in table 3.

**Table 3**
PHYSICAL PROPERTIES OF THE HYDROTREATING CATALYSTS INVESTIGATED.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Size, mm</th>
<th>Form</th>
<th>Bulk density, g/cm³</th>
<th>S BET, m²/g</th>
<th>P e, kg/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO-MoO₃/γ-Al₂O₃</td>
<td>~ 4</td>
<td>spherical</td>
<td>0.69</td>
<td>185</td>
<td>2.6</td>
</tr>
<tr>
<td>NiO-MoO₃/γ-Al₂O₃</td>
<td>~ 4</td>
<td>spherical</td>
<td>0.68</td>
<td>190</td>
<td>2.7</td>
</tr>
<tr>
<td>CoO-MoO₃/γ-Al₂O₃***</td>
<td>3±2</td>
<td>cylindrical</td>
<td>0.67</td>
<td>165</td>
<td>1.7</td>
</tr>
</tbody>
</table>

* P e - mechanical (crushing) strength of the catalysts [4].
** commercial hydrotreating catalyst extruded

Figure 6 represents the content of the active component in the catalyst produced (treated thermally) as a function of its concentration in ammonia aqueous solution. From fig. 6 we found that a certain quantitative relation between them exists independent of types of the AC. This relation can be described by the following formula:

\[ A = \frac{WC_A}{(100 - W)(100 - V) + WC_A} \times 100 \]  

where:
A - content of the active component in the catalyst produced, wt. %;
W - content of the water in the spherical gel, wt. %;
C A - concentration of the active component in ammonia aqueous solution, wt. %;
V - ignition loss of the dry gel, wt. %.

In figure 6, solid lines are depicted based on values calculated by using the above formula (1). The calculation results by using the formula (1) are in good agreement with experimental values. Consequently, we can conclude that the aluminium hydroxide gel do not selectively adsorb the catalytic active component in the ammonia aqueous solution, and the active component is in the concentration equilibrium between the ammonia aqueous solution and water holded in the network structure of the spherical gel.

Figure 7 shows the HDS activities of the catalysts tested for the comparison at 350°C, 3.8MPa and LHSV=4 h⁻¹. In figure 7 the spherical CoO-MoO₃/γ-Al₂O₃ and NiO-MoO₃/γ-Al₂O₃ produced by our granulation method are designated as Cat 1 and Cat 2, and the commercial CoO-MoO₃/γ-Al₂O₃ extruded is designated as Cat 3. A diesel fraction (table 4) derived from the catalytic cracking process is used as a feedstock for hydrotreating tests. From table 3 and figure...
one can clearly see that the mechanical strength and the HDS activities of the catalysts prepared using the granulation method in figure 2 (d) are increased 1.55 times and up to 11 wt. % compared with the mechanical strength and the HDS activity of the commercial catalyst extruded. The better activities of spherical hydrotreating catalysts produced by our granulation method can be explained by the enhanced and regular dispersion of particles of the AC on the surface of the support due to the concentration equilibrium between the ammonia medium and water holded in network structure of the hydrated gel.

Conclusions

In this paper we studied the impregnation of the catalytic AC during the granulation of the Al(OH)₃ gel using the HAM method. By means of the observation about four granulation methods of the pseudosol Al(OH)₃ to the spherical gel in the ammonia aqueous solution in the HAM column, it is identified that the granulation in ammonia medium in which are previously dissolved the active components is better method than other three. During the granulation in the ammonia aqueous solution the aluminium hydroxide gel do not selectively adsorb the catalytic active component and the active component is in the concentration equilibrium between the ammonia aqueous solution and water holded in the network structure of the spherical gel. Also quantitative relationship between the content of the active component in the catalyst produced (treated thermally) and its concentration in ammonia aqueous solution is established. The catalysts for the HDS prepared by the granulation method of the Al(OH)₃ gel in the ammonia medium by using the HAM method show better activities and mechanical strength in comparison with the commercial extruded catalyst for the HDS.

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References


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