

# The Influence of Support Acidity Upon Performances of Hydrogenation Catalysts for Aromatic Hydrocarbons

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*Hydrogenation of benzene, toluene and o-xylene was performed on zeolitic catalysts having as active components palladium or ruthenium. Tested catalytic systems were 1%Pd/ZnH-ZSM-5/Al<sub>2</sub>O<sub>3</sub>, 1%Pd/H-ZSM-5/Al<sub>2</sub>O<sub>3</sub>, 1%Pd/MOR-Cu, 0.5%Ru/ZnH-ZSM-5/Al<sub>2</sub>O<sub>3</sub>, 0.5%Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 0.5%Ru/MOR-Cu and 0.5%Ru/H-ZSM-5/Al<sub>2</sub>O<sub>3</sub>, systems which differs both from type of hydrogenating activity metal and from support acidity. The determination of supports acidity was performed by ammonium thermodesorption method and by volumetric method. Experimental data evidenced that catalytic activity increased with supports acidity increasing in the order ZnH-ZSM-5/Al<sub>2</sub>O<sub>3</sub> > MOR-Cu > H-ZSM-5/Al<sub>2</sub>O<sub>3</sub> >  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, no matter the active component type or aromatic hydrocarbon nature. This thing confirms the spillover effect of hydrogen, in accordance with the fact that in hydrogenation reactions on acid catalytic systems, hydrogen is adsorbed on the metallic component where it dissociates and then migrates to acid centers of the catalyst, where the hydrocarbon molecule is adsorbed and electronically delocalized. Thus it is confirmed that performances of the hydrogenation process are influenced by the support acidity.*

*Keywords : hydrogenation, support acidity, spillover effect*

Restrictions imposed by the environmental norms have lead to a growing in preoccupations regarding decreasing of aromatics content from different industrial solvents [1,2,3] and from automobile fuels. Specialty literature studies a large domain of catalytic support, different both from nature of metallic component and from supports used at preparation of these catalytic systems.

Between active metal components, the most used were nickel, palladium, platinum, molybdenum, wolfram and ruthenium, in monometallic, bimetallic or promoted catalytic systems [4-8]. The catalytic supports preferred by different authors were:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, MCM-41, TiO<sub>2</sub>, H[Al]ZSM-5, CeO<sub>2</sub>, ZrO<sub>2</sub> [5,6,9,10-14].

Other authors have tried to determine the influence of support acidity upon the hydrogenation reaction of aromatic hydrocarbons, preparing supports based on alumina and zeolite of faujasit type [15], individual supports or their combinations in different proportions, by using as active metallic component palladium or platinum. There were used also Y (8,1) zeolites, with a ratio silica/aluminum =8.1, Y (6,8), with a ratio silica/aluminum =6.8, or mordenite, simple catalytic systems, without an active metallic component, which lead to low performances for the hydrogenation reaction of benzene and to a decreasing in a short time of the hydrogenation catalytic activity [16].

In this paper there are presented the results obtained by benzene, toluene and o-xylene hydrogenation on different catalytic systems.

Hong Yang, Honglin Chen and others studied naphthalene hydrogenation on catalysts of type Pt/zeolite KA and Pt/zeolite KA + zeolite HY +  $\gamma$  alumina [17], or Pt/RHO and Pt/RHO + zeolite HY [18], obtaining higher conversions in case of hydrogenation on the catalyst having in composition HY zeolite. This behaviour is explained for a spillover mechanism according to the hydrogenation reaction takes place by hydrogen adsorption on the metallic component, where it dissociates, followed by migration to acid centers of the zeolitic support, where the hydrocarbon molecule is

adsorbed and electronically delocalized. In this way, hydrogenation takes place much easier.

The same authors have studied the hydrogenation reaction of 1-hexene by using two catalysts based on platinum, one of Pt/CMS type (carbonic molecular sieve) and another of Pt/CMS+zeolite HY type [19], results being much better in case of using zeolitic catalyst. Another active metal, rhodium deposited onto alumina was studied for toluene hydrogenation reaction by using the catalyst as such or in mixture with different supports, silicon dioxide, active coal or zeolite HY [20]. Concentration to acid centers was determined by TPD (programmed thermodesorption), acid strength varying in order HY >> C<sub>active</sub> > Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>. Experimental results lead to a much better behaviour of the catalytic system including zeolite of type HY and authors explain this behavior because of the spillover mechanism of hydrogen for the hydrogenation reaction.

This paper proposes to verify this mechanism by influence of different catalytic systems acidity upon benzene, toluene and o-xylene hydrogenation by using as active components palladium or ruthenium.

## Experimental part

In order to demonstrate the influence of support acidity upon the activity of hydrogenation catalysts, there were prepared by impregnation a series of monometallic catalysts based on palladium or ruthenium, by using different supports, different by acidity. The achievement of the hydrogenation reaction in fixed catalytic bed assumed the use of granular catalysts, such as the preparation of catalysts deposited on alumina, on zeolite with alumina, on modified zeolite bind with alumina, or on mordenite copper form, needed in the first step the granulation of catalytic supports by extrusion.

Alumina used as binder for preparation of catalysts based on synthetic zeolites is a hydrated alumina. The catalytic support based on alumina was prepared by binding a reformation alumina with Klauss alumina. All the catalytic precursors used for supports preparation are as powdery.

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**Table 1**  
PREPARATION OF CATALYTIC SUPPORTS

No.	Type of catalytic support	Solid precursors*	Weight ratio	Binding agent	Proportion binding agent to solid (cm <sup>3</sup> sol./g solid)	Mixing time (min.)
1.	ZnH-ZSM-5 binded with alumina, (2 % Zn)	ZnH-ZSM-5/ alumina	1/1	Aqueous sol. 10% HNO <sub>3</sub>	0,55	80
2.	MOR-Cu binded with alumina, (2 % Cu)	MOR-Cu/ alumina	1/1	Aqueous sol. 10% HNO <sub>3</sub>	0.55	80
3.	γ - alumina	Alumina 1**/ alumina 2***	1/1	Aqueous sol. 10% HNO <sub>3</sub>	0.40	60
4.	H-ZSM-5 binded with alumina	H-ZSM-5/ alumina	1/1	Aqueous sol. 10% HNO <sub>3</sub>	0,51	60

\*solid precursors as powders

\*\* alumina purified by treatment with azotic acid

\*\*\*alumina precipitated by treatment with ammonium carbonate

The preparation of supports from precursors as powdery assumes binding operation by mixing, to bring in form there was made the paste extrusion obtained by mixing, followed by drying and calcinations to achieve a convenient mechanical resistance. Mixing was achieved by using a masticator made of stainless, thermo stated steel, of 1 liter capacity, foreseen with two helicoidal horizontal screws, made also of stainless steel and they rotate with a constant rate. Binding of supports as powdery was made by using a 10% solution of nitric acid.

Extrusion of mixed paste was made by means of a manual pressing extruder made of stainless steel, with a capacity of 200 cm<sup>3</sup>, with nozzle having a diameter of 3 mm. Drying of extruded items was performed in a thermostated oven at 120 °C during 6 h. Calcinations of extruded items were made in a thermostated oven, at 550 °C, during 6 h.

Preparation procedures of catalytic supports are presented in table 1, and their characteristics are presented in table 2. Catalytic supports of type ZnH-ZSM-5 binded with alumina and MOR-Cu binded with alumina have a content of approximately 2% Zn, 2% Cu, the metal being introduced in the crystalline network of zeolite from the crystallization phase, in presence of a templation matrix.

Catalysts tested in this study were 1%Pd/ZnH-ZSM-5/Al<sub>2</sub>O<sub>3</sub>, 1%Pd/H-ZSM-5/Al<sub>2</sub>O<sub>3</sub>, 1%Pd/MOR-Cu, 0.5%Ru/ZnH-ZSM-5/Al<sub>2</sub>O<sub>3</sub>, 0.5%Ru/γ-Al<sub>2</sub>O<sub>3</sub>, 0.5%Ru/MOR-Cu and 0.5%Ru/H-ZSM-5/Al<sub>2</sub>O<sub>3</sub>. Metal content was between 0.98-1.03 % weights for catalysts based on palladium and between 0.51-0.54% weight for catalysts based on ruthenium.

Catalytic activity of prepared catalysts was tested in the hydrogenation reaction of benzene and o-xylene for the catalysts based on palladium and catalysts based on

**Table 2**  
PHYSICAL-CHEMICAL CHARACTERISTICS OF CATALYTIC SUPPORTS

No.	Type of catalytic support	Density (g/cc)	Specific area (m <sup>2</sup> /g)	Mechanical resistance (kf/cm <sup>2</sup> )	Acidity (mechiv/g)
1	Zeolit Zn H-ZSM-5 binded with alumina	0.588	306.7	13.76	0.730*
2	MOR-Cu binded with alumina	0,809	295.46	15,24	0,61*
3	γ-alumina	0.585	183.7	9.21	0.009**
4	H-ZSM-5 binded with alumina	0,580	208	11,55	0,38*

\*determination by the method of ammonia thermodesorption

\*\* determination by volumetric method

ruthenium were tested in the hydrogenation reaction of benzene and toluene. Feeding composition of the hydrogenation reactor was of 10% (vol.) aromatic component and 90% (vol.) hexane.

Reaction conditions for catalysts based on palladium were:

- pressure, 10 bar;
- temperature, 150°C;
- volume rate of aromatic component, 0.2 h<sup>-1</sup>;
- molar ratio hydrogen/aromatic component, 10/1.

Catalysts based on ruthenium 0.5%Ru/ZnH-ZSM-5/Al<sub>2</sub>O<sub>3</sub>, 0.5%Ru/MOR-Cu, 0.5%Ru/H-ZSM-5/Al<sub>2</sub>O<sub>3</sub> and 0.5%Ru/γ-Al<sub>2</sub>O<sub>3</sub>, were tested on a larger temperature interval: 30-110°C. Characterization of the reaction products was performed by chromatography, the results of the hydrogenation process being expressed by conversion to the total saturated component.

## Results and discussion

The results of the activity tests are presented in figure 1, in function of the acidity of the support used for the catalyst preparation, for catalysts based on palladium. In figures 2,3 there is presented the influence of support acidity upon benzene or toluene hydrogenation, for the temperature interval mentioned above.

From figure 1 there is observed a decrease of catalytic activity with the increase of acidity of support used for the catalyst preparation, both for benzene hydrogenation and for o-xylene, the content of active component being approximately the same (1% weight). The highest conversion is assured by the modified support of type

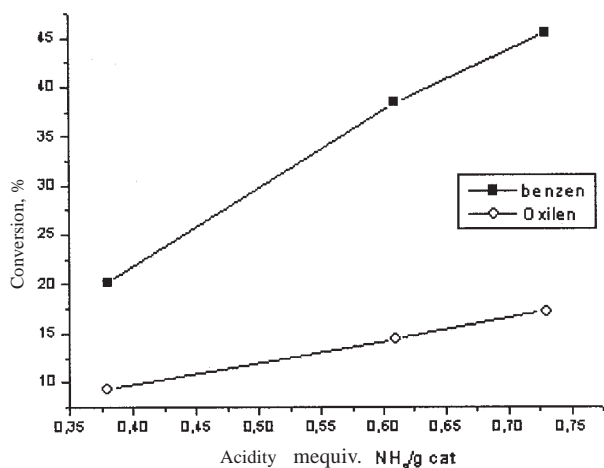


Fig. 1. Variation of benzene and o-xylene conversion in function of support acidity for hydrogenation on palladium catalysts

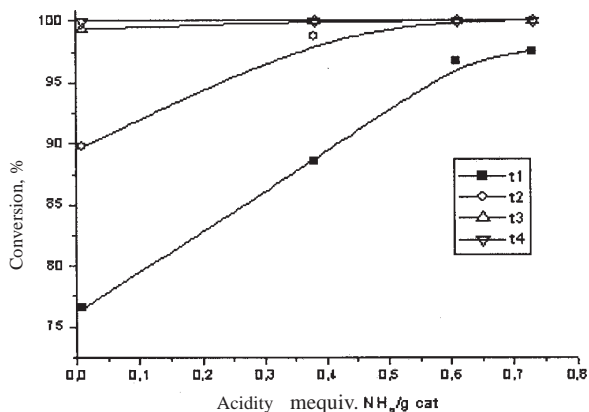


Fig. 2. Variation of benzene conversion in function of support acidity for hydrogenation on ruthenium catalysts at t<sub>1</sub>=30°C, t<sub>2</sub>=60°C, t<sub>3</sub>=90°C, t<sub>4</sub>=110°C

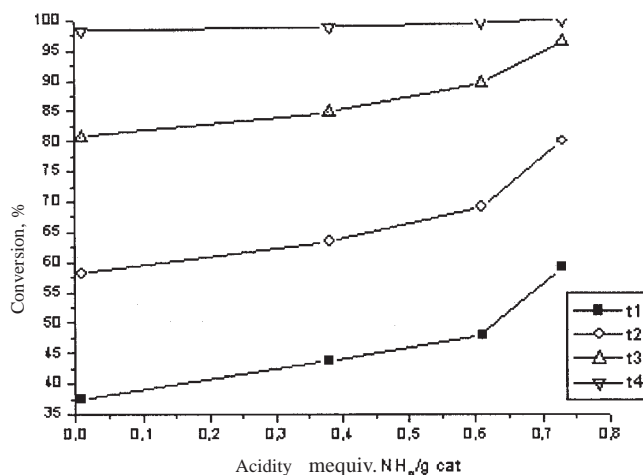


Fig. 3. Variation of toluene conversion in function of support acidity for hydrogenation on ruthenium catalysts at t<sub>1</sub>=30°C, t<sub>2</sub>=60°C, t<sub>3</sub>=90°C, t<sub>4</sub>=110°C

Zn-ZSM-5, binned 1/1 with γ-Al<sub>2</sub>O<sub>3</sub> (45.42 % for benzene and 17.21 % for o-xylene). This support has the highest total acidity (0,73 mequiv. NH<sub>3</sub>/g cat.).

At the opposite part there is situated the catalyst deposited on H-ZSM-5/Al<sub>2</sub>O<sub>3</sub> with a conversion of 20.15 % for benzene and 9.31 % for o-xylene, this support having the lowest total acidity of 0.38 mequiv. NH<sub>3</sub>/g cat. The other physical-structural characteristics of the support can present an influence upon the catalytic activity: specific area pore volume, distribution of acid centers strong behaviour.

Ruthenium deposited on zinc modified zeolite (0,73 mequiv. NH<sub>3</sub>/g cat) and on mordenite copper form (0.61 mequiv. NH<sub>3</sub>/g cat) assures benzene conversion over 96%, even at room temperature and at 60°C conversion is of 100%. At low temperatures ruthenium deposited on γ-Al<sub>2</sub>O<sub>3</sub> (support with the lowest total acidity- 0.009 mequiv/g cat.) lead to much smaller conversions of benzene compared to the other supports.

When temperature increases, the difference between performances of the four catalysts decrease and at 110 °C all catalysts give benzene conversion of 100% (fig. 2).

The same aspect is present for toluene hydrogenation (fig. 3), the increase of support acidity leads to the increase of toluene conversion, with the difference that there is obtained much lower conversion than for benzene. Because γ-alumina represents a half from zeolitic catalysts weight these aspect assuring binding for granules profiles of finite catalyst, but zeolites and their modified forms, zinc and copper giving the acidity of zeolite catalysts, even for their low quantities (approximately 2%), highlighting this character. This behaviour of catalytic activity increasing with the support acidity growing can be explained as a good mobility of dissociate adsorbed species in one phase, named donor, on another phase, named acceptor. In this way, an apparently inert material can have catalytic activity.

"Spillover" effect, specific to metals deposited on acid supports, accentuates the hydrogenation catalytic activity, with very good performances in the present case when ruthenium was used as active component. The increase of support acidity up to a limit, accentuates the "spillover" effect. In this way there can be stated that the acidity of the catalytic support influences the catalyst performances for the hydrogenation reaction of aromatic hydrocarbons.

## Conclusions

Experimental investigations evidenced the following general observations:

- the acidity of catalytic support influences performances of hydrogenation catalysts, the increase of acidity leading to an increase of aromatic hydrocarbons conversion (benzene, toluene, o-xylene);

- the influence of support acidity is stronger manifested at low temperatures;

- hydrogenation of monocyclic aromatic hydrocarbons on catalysts with an acid character, follows a "spillover" mechanism, where hydrogen adsorbs and dissociates on metallic centers, from where migrate on acid centers, where it is adsorbed and electronically delocalized the molecule of aromatic hydrocarbon;

- spillover type mechanism is present whatever metallic component type or nature of aromatic hydrocarbon involved in the reaction.

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