

Metal clusters in zeolite 4A obtained by synthesis process

E. David*

National Research Institute of Cryogenics & Isotope Technologies
P.O.Box 10, Rm.Valcea, Code 240050, Romania

* Corresponding author: E-mail address: david@icsi.ro

Received in revised form 15.07.2006; accepted 30.09.2006

Materials

ABSTRACT

Purpose: The goal of this paper is to study the possibility of obtaining of the supported metal clusters in zeolite 4A that are a new class of composite materials with application in sorption and catalytic processes.

Design/methodology/approach: The materials were fabricated by synthesis process involving organo-metallic chemistry on surfaces, gas-phase cluster chemistry and chemistry in zeolite cages. The magnesium clusters in zeolite 4A(Mg/Z4A) has been prepared by ion exchange, followed by calcination and reduction processes. The metals are introduced as cationic form, which replace cations such as sodium from zeolite and then treated by heating in oxidized mixture or air and reduced in hydrogen. The activation and reduction treatments give the highest metal dispersions. The texture studies, X-ray diffraction, transmission electron microscopy (TEM) and atomic absorption were used for to characterize these materials.

Findings: Through this study it was determined the structures and properties of (Mg/Z4A) composites and then these properties were compared with zeolite 4A properties without metal addition. It was found that Mg/Z4A have new properties, with high catalytic effect and the reducing process are decisively regarding the size and the placement of the metal magnesium particles into zeolite 4A.

Research limitations/implications: It is noticed, that increase of the reducing temperature over 600°C promotes the forming of metal clusters with great sizes at the external surface of zeolite 4A and the catalytic activity is diminished. The activation and reduction treatments give the highest metal dispersions, but the most uniform metal clusters are not easily formed.

Practical implications: Obtained results allowed to optimize the catalytic activity of the supported metals on zeolite.

Originality/value: This work contains several new aspects, which are: the conditions for performing the magnesium metal clusters in zeolite 4A cages, wide range of investigated materials and combining the microstructure of the material with the susceptibility of the formation of the metal clusters in zeolite 4A surface. Also, composite materials have been obtained following a simple and low-cost route.

Keywords: Metal clusters; Zeolite 4A; Magnesium oxide; Magnesium

1. Introduction

While most industrial applications of zeolites make use of these materials in their acid mode, zeolites are also excellent supports for metals [1,2]. The importance of the zeolites can be attributed to their high surface areas in combination with their chemical nature. The industrial zeolite 4A is crystallized from the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and is an excellent support for

metals, performing together materials which contain as acid states as metallic clusters (mono or multimetallic). These materials behave as bifunctional catalysts. The metals laid down on zeolites confer the selective form of the material [3-5]. The zeolites are defined as aluminosilicates having a structure with channels or cavities able to accept gas molecules [6]. In these channels or cavities can be deposited basic or transition metals, which together with the zeolite matrix form a material with new

properties [7-9]. These resulted from the combination of the properties of the zeolite with the physical and chemical properties of the incorporated metal [10-12]. Routes for preparation of molecularly or ionically dispersed metal clusters on supports include (i) deposition from solution, (ii) reaction with the support surface, and (iii) synthesis from metal precursors on the support surface. Zeolite supported metal clusters have most commonly been prepared by ion exchange followed by calcination and reduction [13-14]. Usually the metals are introduced as cationic form, which replace cations such as sodium in zeolite and then decomposed by heating in oxidized mixture or air and reduced in hydrogen. The activation and reduction treatments give the highest metal dispersions, but the most uniform metal clusters are not easily obtained [11]. The study of the systems metal clusters/zeolite refers to the possibility of introducing by metal and its dispersion into framework structure of zeolite. Some authors reported that the growth of metal particles into zeolite cavities can induce a local destruction of the matrix [1,4,8,11]. After reducing at high temperature an important part of metal is present as particles which are greater than the zeolite cavities. These particles are located in voids created into zeolite, leading to the significant diminution of its crystalline form [12,14]. The purpose of this work is to present the results regarding the investigations on the structure and properties of the magnesium clusters that have been prepared in zeolite 4A (Mg/Z4A) and the possibility by using of these materials in the catalytical processes [15-18]. The important opportunity in mass transfer process may be to find reactions for which the activity or selectivity of supported metal clusters is superior to those of conventional supported metals.

2. Experimental

Formation of the metal magnesium clusters in zeolite 4A cages involves the introducing in zeolite, used as matrix, of metal magnesium.

2.1. Zeolite 4A manufacturing

Zeolite 4A is not known in the nature as a mineral and is obtained by hydrothermal synthesis from alkaline gels and aluminosilicates. Its usual shape is in sodium, but through different ways can be obtained other cationic shapes of the mono, di or trivalent metals. Zeolite 4A was obtained from the mixture of sodium silicate, sodium aluminate, sodium hydroxide, water and natural kaolin by uniform mixing. The composition was put in a crystallizer tank and held for a few hours at a temperature of about 100°C. Thus, there were obtained zeolite crystals, which were separated from the base solution by a vacuum filter.

The crystals obtained in this way are usually very small (their dimension does not exceed a few microns) may be said that a fine crystal powder was obtained, which is inconvenient for practical use. That for, after obtaining the crystals, their granulation was performed. For this it is added a small quantity of kaoline as binder and then extruded to 2-6 mm cylindrical pellets in a pneumatic press. The obtained zeolite crystals are saturated with water, which are removed through heating the zeolite at a temperature of about 650 °C. In this way is also

achieved the activation of the material. After the thermal processing the framework of the zeolite becomes resistant to the action of the mechanical and thermal agents. In sodium form, the zeolites don't possess acid sites. Through replacing the Na⁺ ions by other ions with more valences, the zeolites are transformed in catalysts, which present active centers with acid characters.

2.2. Mg/Z4A composites preparation

The Mg/Z4A composites were prepared from zeolite 4A, as matrix and a soluble salt (magnesium acetate) as the precursor of the metal. Figure 1 shows the processing flow of composites.

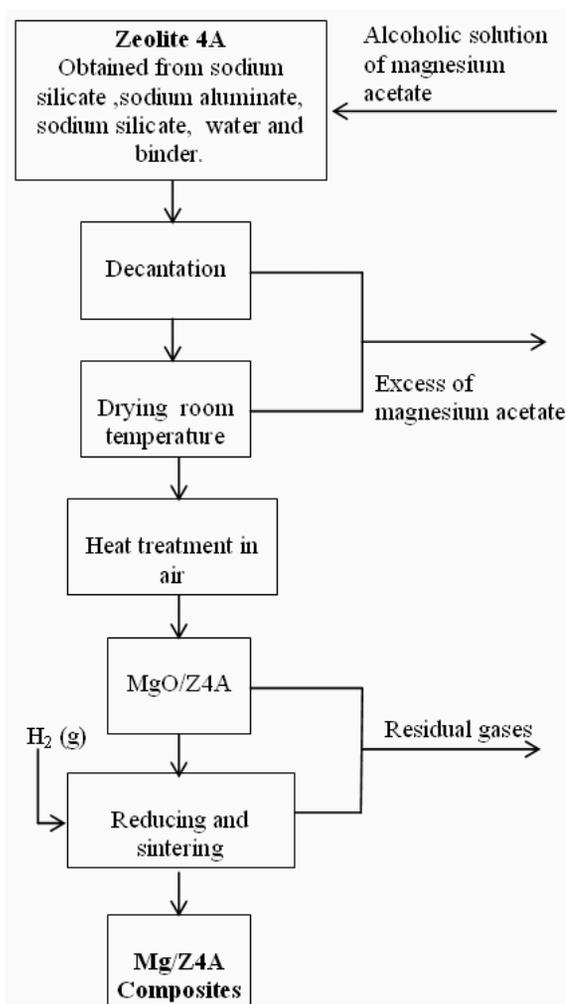


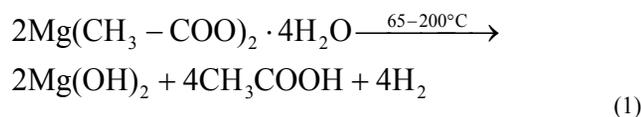
Fig. 1. The Mg/Z4A producing flow using zeolite 4A as matrix and magnesium acetate as metal precursor

The method used for depositing of the metal into the cavities of zeolite was the impregnation, followed by the calcination, reducing and sintering with hydrogen. The impregnation of zeolite 4A was performed with an alcoholic solution of magnesium acetate of 10 wt%, for 20 hours at the room temperature and for 4 hours at 65 °C.

It was used a three times greater volume than the total volume pores of the zeolite. The excess of solution was removed by decantation and then drying at room temperature for 4 hours. The material was subjected to a heat treatment in an air flow after the following cycle: one hour for each temperature of 65, 100, 120, 150 °C; two hours for 200 and 250 °C; four hours for 300 °C and six hours for 350 °C. Under these conditions the magnesium acetate is decomposed in magnesium oxide and have formed MgO/Z4A. A sample of this material was subjected to the determination of the mechanical and thermal resistance. Subsequent MgO/Z4A was subjected to a special treatment of reducing with hydrogen of the magnesium oxide till metal magnesium scattered into the mass of zeolite. The reducing time was of 6 hours, the H₂ flow rate was constantly, it assured in the free section of the reactor, a gas speed of 0.012ms⁻¹. It was determined the total magnesium content from the samples through atomic absorption with an analyzer Pye Unicam. The properties and characteristics of the samples MgO/Z4A and Mg/Z4A were compared with the zeolite 4A without magnesium addition.

3. Results and discussions

The physical structural characterisation of the resulted composites indicates the predominant formation of clusters. The calcination of the material is done to remove the water and the ligands from zeolite. The magnesium acetate is decomposed in magnesium oxide after the following chemical reaction:



Thus, the zeolite loaded with metal ions is heated in a high flow of air. Three phenomena accompany the elimination of water:

- (i) Autoreduction (formation of metal clusters and zeolite protons in the reducing atmosphere – decomposing). Under calcination conditions, the reduction to metal clusters is followed by their growth and the formation of oxide particles. These particles, in turn, can react with protons to form metal ion and water. Uncontrolled autoreduction is often undesired, because agglomeration of clusters to larger particles can take place;
- (ii) Ion migration to smaller zeolite cages, which can be prevented by limiting the temperature of calcination of about 350°C;
- (iii) Ion hydrolysis leads to dissipation of positive charge of the material. The reducing takes place according the following chemical reaction:



and after reducing an important part of metal is present into zeolite as particles.

The studies performed by X-ray diffraction, transmission electron microscopy (TEM) and texture studies pointed out the modifications that appeared in the physical and chemical properties of the composites obtained through magnesium addition in the framework of zeolite 4A.

The crystalline framework of the zeolite 4A is enough rigid and therefore stable at temperature. In sodium form, as it results usually from synthesis, it has not acid centers. Thus the zeolite framework can be presented schematic like in figure 2:

Table 1

Variation of some properties of zeolite 4A in different cationic forms

No. of cations in the elementary cell	Density (ρ, g/cm ³)	Parameter of elementary cell a ₀ (Å)	Cation radius r _c (Å)
12 Na ⁺	1.99	12.32	0.98
4Mg ²⁺ 4 Na ⁺	2.04	12.29	0.65

Table 2

Structural characteristics and distribution of the pore volume for Z4A, MgO/Z4A and Mg/Z4A samples

Material	Sample 1 (Z4A)	Sample 2 (MgO/Z4A)	Sample 3 (Mg/Z4A)
Specific surface, S _{Langmuir} (m ² /g)	211.20	201.50	151.20
Apparent density (ρ _a , g/cm ³)	1.99	2.04	2.14
Vol. of pores (0-300 Å) (V _p , cm ³ /g)	0.2207	0.1752	0.1927
Vol. of pores (> 300 Å) (V _p , cm ³ /g)	0.2288	0.2381	0.2177
Volumes total of pores (V _t , cm ³ /g)	0.4493	0.4133	0.4104

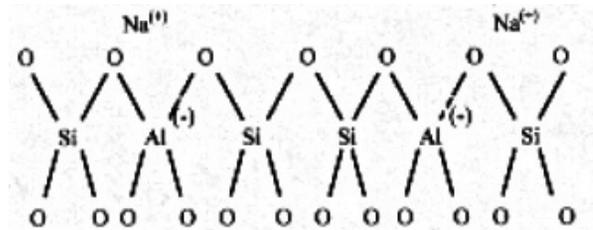


Fig. 2. Zeolite framework in sodium form

By replacing the Na⁺ ions with Mg²⁺ ions, the zeolite changes in a new material which presents active centers with acid character. The divalent cations are bound by the two valences at unequal distances which leads to a not uniform repartition of the charge, one of the tetrahedrons is neutralised completely and the other one remains with a partial negative charge, as shown in the schematic representation from figure 3.

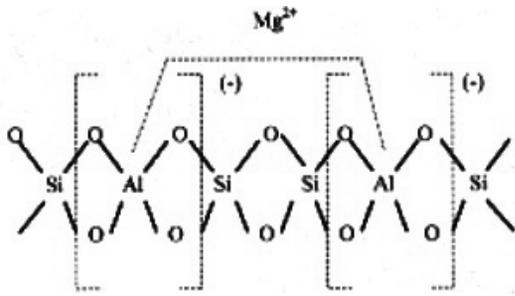


Fig. 3. Zeolite framework in magnesium form

The introducing of magnesium in framework of the zeolite modifies its properties. In tables 1, 2 and figure 4 are presented some of the appeared modifications:

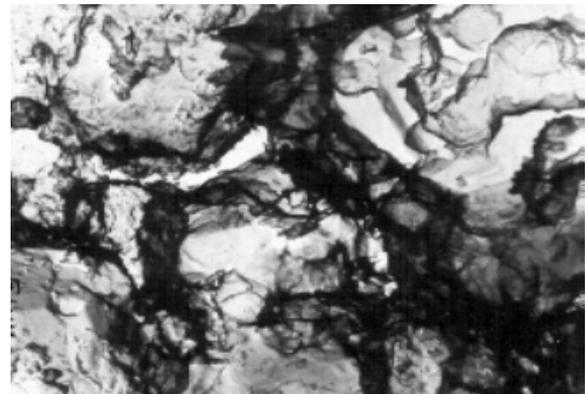
It was found that the density of zeolite 4A increases when is introduced magnesium in its mass, the entire water quantity is drawn out from framework of the zeolite, the size of the cubic elementary cell remains almost constant, and in the structure of the zeolite it has been observed a low contraction of the crystalline framework. The thermal treatment prior reducing Mg^{2+} to Mg^0 , as well the conditions of the reducing process are decisively regarding the size and the placement of metal particles. It has been ascertained that at low reducing temperatures, smaller size metal particles are formed, but the reducing percentage is low. At high temperature the metal atoms migrate to the external surface of the zeolite and form crystalline aggregates. However frequently the crystalline aggregates can also appear under mild reducing conditions, that proves that the reducing of metal cations in order to obtain a zeolite with dispersed metal represents a process of distinct complexity. The magnesium content from the mass of the zeolite was determined to be 4.28 wt%. It was also performed a texture study of these materials (see data from table 1 and 2).

The investigations through transmission electron microscopy (TEM) were performed with an analyzer TESLA – BS 540. The samples were treated through negative retorting with carbon.

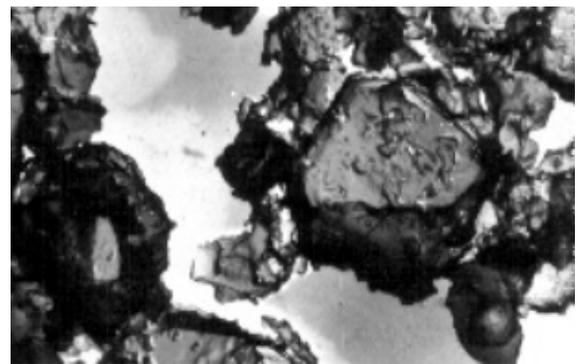
These investigations point out the existence in the samples of well crystallised particles, with the size of 1-5 μm or even greater, having the most important share and representing the support, see figure 4a. On their surface or isolated, with a low volume share appear submicron particles. In all samples appears a stage near to amorphous, insoluble in fluorhydric acid, with tendency, of agglomeration in the channels or cavities of the zeolite (fold retorts) more accentuated aspect at sample Mg/Z4A (see figure 4 c)

At the sample Mg/Z4A in contrast with the samples Z4A and MgO/Z4A there is observed the presence of some cubic formations, well crystallised and opaque at the fascicle, with the sizes between 0.1 and 0.3 μm (indicated with arrows in photo(c) from figure 4. These formations can be considered metal clusters resulted from the support in the moment of dissolving in acid of the retorted preparation.

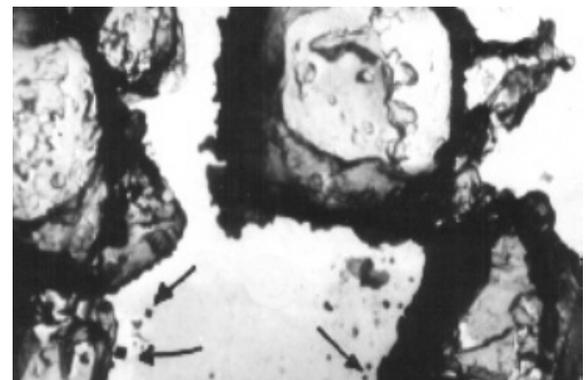
Such formations, but smaller, to amorphous are aggregated in the pronounced irregularity zone of the faces of the granules, the possibility of detaching having only the most developed; the "amorphous" phase remains fixed on the retort and produces an increasing of the capacity in the intergranular zones, specific for sample (Mg/Z4A).



(a)



(b)



(c)

Fig. 4. Transmission electron microscopic picture (bottom magnification 7000x) of Z4A (a); MgO/Z4A(b); and Mg/Z4A(c)

The experimental results of the texture study (specific surface, volume of the pores, their distribution depending on the radius size) are presented in table 3 and 4.

Sample 1 which represents zeolite 4A (Z4A) promotes all the three types of pores; micro, mezo and macropores, the maximal distribution being situated in the range of rays between 1000-10000 \AA . Working in the approximation of the cylindrical pores the average radius of the pores is 42.55 \AA .

By introducing MgO in zeolite 4A, the specific surface and the volume of pores decreases from 211 m^2/g to 201.5 m^2/g , and

from 0.4493 cm³/g to 0.4133 cm³/g, being affected the pores which radius smaller than 10Å, which are partly blocked, their volume decreasing to the half. The development of the porosity in the range of radius 15-25Å, indicates the building up of same clusters, concrescences which form proper channels.

The average radius of the pores remains practically unchanged. The reducing of magnesium oxide with hydrogen till magnesium is associated by the decreasing of the specific surface till 151 m²/g, decrease owing to the obturation of micropores by the metallic magnesium clusters. Their volume of micropores decreasing to 0.00981 cm³/g; 3.24 times smaller than in the support.

The growing metal particles inside zeolite cages can induce a local destruction of the matrix, as depicted schematically in fig. 5.

After reduction at high temperatures, a significant portion of the metal is present as particles that are larger than the zeolite cages. These particles are located in voids created within the zeolite matrix. This phenomenon created a significant loss in zeolite crystallinity when metal reduction was carried out over 600°C.

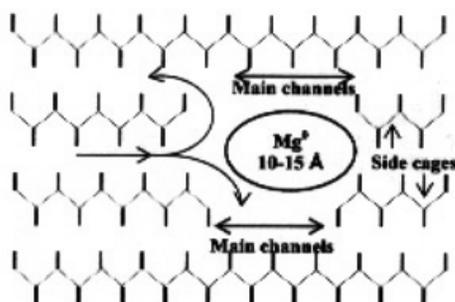


Fig. 5. Transport pathways opened by local destruction of zeolite 4A channels caused by growing Mg⁰ particles

Table 3
Distribution of volume pore as function of pore size diameter

Pore size diameter (Å)	Distribution of vol. pores V _p (cm ³ /g)		
	Z4A	MgO/Z4A	Mg/Z4A
Pore size diameter (Å)			
5≤10Å	0.0318	0.0177	0.0098
>10≤15Å	0.0169	0.0148	0.0199
>15≤25Å	0.0210	0.0688	0.0331
>25≤50Å	0.0637	0.0182	0.0387
>50≤100Å	0.0527	0.0262	0.0602
>100≤300Å	0.0346	0.0298	0.0302
>300≤1000Å	0.0152	0.0187	0.0175
>1000≤10000Å	0.2070	0.2100	0.1972
>10000Å	0.0060	0.0090	0.0063
S _{hysteresis} (m ² /g)	23.67	30.82	16.97
Average radius (Å)	42.55	41.02	54.28

Table 4
Distribution of pores' volume depending on radius size

Sample	Volume of pores, V _p (cm ³ /g)		
	Z4A	MgO/Z4A	Mg/Z4A
Micropores(R≤15Å)	0.0487	0.0325	0.0297
Mesopores(15 > R≤1000Å)	0.1876	0.1618	0.1807
Macropores(R>1000Å)	0.213	0.219	0.200

The decreasing of the volume micropores reduces the adsorption properties of the zeolite 4A and transforms it into a material with high catalytic properties, owing Mg⁰ particles which are dispersed into zeolite.

The average radius of the pores increases gently from 42.55 Å for Z4A to 54.28 Å for Mg/Z4A (see table 3). The classification of the pores depending on the size of their radius for Z4A, MgO/Z4A and Mg/Z4A and the distribution of the volume pores are presented in table 4.

Beside appeared modifications in the porous structure the thermal resistance increases to ~ 1500°C for MgO / Z4A and ~800°C for Mg/Z4A. Till these temperatures the composites do not modify significant their properties.

Estimating the catalytic performances, it has been found that in a mixture of gases containing 2.35 vol.% CO in N₂, which pass through a catalytic bed of Mg/Z4A, carbon monoxide is reduced to carbon. The temperature was between 200-400°C. The reactor containing Mg/Z4A was heated to ~ 350°C and then vacuumed at ~ 10⁻² torr for 10 minutes, after which it was brought to the working temperature. The gas pressure in the reactor was with 0.2 bar greater than the atmospheric pressure. The content of carbon monoxide from initial mixture and the sample of the product was analysed by G.C. with a thermal conductivity detector - Hewlett Packard. Figure 6 shows that the concentration of carbon monoxide decreases for about 15 minutes and then remains at a constant value (see curve 1). The Mg/Z4A adsorbs the carbon monoxide (figure 6, curve 2) while the nitrogen passes through the adsorber without significant quantities being adsorbed and thus can be separate of carbon monoxide.

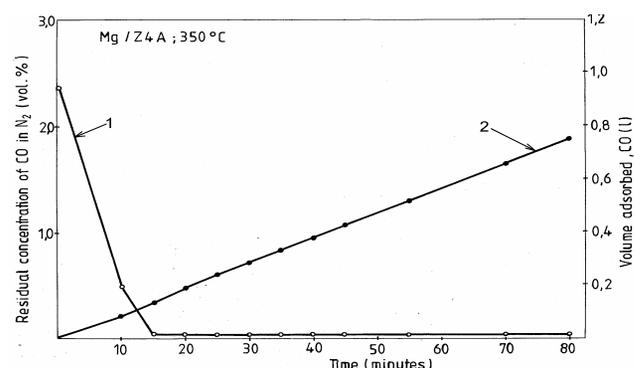


Fig. 6. Variation of the carbon monoxide concentration in nitrogen and adsorbed volume of carbon monoxide in time by Mg/Z4A at 350°C after crossing of the mixture gas through catalytic bed

The maximum quantity of CO removed from nitrogen was of 3.35 wt.% at 350°C. The samples of MgO/Z4A that were reduced with hydrogen under 600°C, although having a lower metal dispersion were twice as active as identical samples reduced over 600°C.

4. Conclusions

Through addition of magnesium into the mass of zeolite 4A has been obtained Mg/Z4A composites with new properties. The

reducing process are decisively regarding the size and the placement of the metal magnesium particles. It has been found that at reducing temperatures under 600°C smaller size metal particles are formed, but the reducing percentage is low. Magnesium clusters larger than the zeolite cages and dispersion was distinctly higher in the sample reduced over 600°C.

With carbon monoxide reducing at carbon, as catalytic sample it was found that the sample which was reduced under 600°C, although having a lower metal dispersion were twice as active as identical sample reduced over 600°C. The catalytic activity of the Mg/Z4A are given by the clusters or atoms of magnesium dispersed into the mass of the zeolite. The reducing temperature with hydrogen may not exceed 600°C, because it would promote the forming of clusters or metal particles with great sizes at the external surface and the catalytic activity is diminished.

References

- [1] H.D. van Heijnsbergen, G. von Helden, M.A. Duncan and G. Meijer, "IR-REMPE Spectroscopy of magnesium oxide clusters," *J. Chem. Phys.* 116 (2002) 2400-2408.
- [2] T.M. Ayers, J.L. Fye, Q. Li and M.A. Duncan, "Synthesis and isolation of titanium metal cluster complexes and ligand-coated nanoparticles with a laser ablation flowtube reactor," *J. Clus. Sci.* 14, 97 (2003) 97-105.
- [3] A. Jain, V. Kumar, M. Sluiter, Y. Kawazoe, First principles studies of magnesium oxide clusters, *Journal Computational Materials Science* 36 (2006) 171–175.
- [4] O.Y. Vassilyev, G.H. Hall, J.G. Khinast, Modification of zeolite surfaces by Grignard reagent, *J.P. Materials*, Vol. 13, No. 2, (2006) 5-13.
- [5] Y. Du, Y. Sun, Y. Di, L. Zhao, and all., Ordered mesoporous sulfated silica-zirconia materials with high zirconium contents in structure, *J.P. Materials*, Vol. 13, No. 2, (2006) p.163.
- [6] K. Konopka, M. Wodzinski, M. Szafran, Fabrication of Al₂O₃-Al composites by infiltration method, *Proceedings of 12th International Scientific Conference, AMME'03, Gliwice-Zakopane 2003*, 491-495.
- [7] T. Ohgushi, S. Komarneni, A.S. Bhalla, Mechanism of microwave heating of zeolite A, *Journal of Porous Materials*, Vol. 8, No. 1, (2001) 23-37.
- [8] B. Li, L. Wang, Q. Jin, and all, Theoretical studies of metal clusters in zeolite Y, *Journal of Porous Materials*, Vol. 9, No. 4, (2002) 287-291.
- [9] Y. Goto, Y. Fukushima, P. Ratu, Y. Imada, and all., Mesoporous material from zeolite, *Journal of Porous Materials*, Vol. 9, No 1, (2002) 43-49.
- [10] W.J. Wang, H.Y. Lin and Y.W. Chen, Carbon monoxide hydrogenation on Cobalt/Zeolite catalysts, *Journal of Porous Materials*, Vol. 12, No 1, (2005) 5-13.
- [11] P. Gallezot, *Metal Clusters in Zeolites*, Metal Clusters, ed., Wiley, New York, ch. 8, 1986.
- [12] H.P. Cheng, and D.E. Ellis, Electronic structure, binding energies, and interaction potentials of transition metal clusters, *J. Chem. Phys.* 95, (1990) 3735-3747.
- [13] G. Pető, G.L. Molnár, Z. Pászti, O. Geszti, A. Beck and L. Guzzi, Size dependent electronic structure of gold nanoparticles deposited on SiO_x/Si(100), *Materials Sci. and Eng.*, C19 (2002) p.95.
- [14] L. Guzzi, A. Beck, A. Horváth and D. Horváth, From molecular clusters to metal nanoparticles, *Topics in Catalysis*, 19, (2002) p.157.
- [15] T. Visser, T.A. Nijhuis, A.M.J. van der Eerden, K. Jenken, Y. Ji, W. Bras, S. Nikitenko, Y. Ikeda, M. Lepage and B.M. Weckhuysen, Promotion effects in the oxidation of CO over zeolite-supported Pt nanoparticles, *J. Phys. Chem. B* 109 (2005) 3822-3831.
- [16] J.A. Delgado, T.A. Nijhuis, F. Kapteijn, and J.A. Moulijn, Determination of adsorption and diffusion parameters in zeolites through a structured approach, *Chem. Eng. Sci.* 59 (2004) 2477-2487.
- [17] A.J. Evans, R.M. Ormerod, V.L. Zholobenko, Redox properties of silver incorporated zeolites, *Proceedings of the 13th International Zeolite Conference, Recent Research Report, Montpellier*, (2001) 30-37.
- [18] R.J. Davis, New perspectives on basic zeolites as catalysts and catalyst supports, *J. Catalysis*, 216 (2003) 396-405.