A Comparative Study of M/ZSM-5 (M = Pd, Ag, Cu, Ni) Catalysts in the Selective Reduction of Nitrogen (II) Oxide by Ammonia

Marzieh Hamidzadeh[1,2], Mitra Ghassemzadeh [1*], Aliakbar Tarlani[1], Saeed Sahebdel Far[2]

[1] Chemistry and Chemical Engineering Research Center of Iran, Tehran, Iran

* [2]Catalyst Research Group, Petrochemical Research and Technology Company, National Petrochemical Company, Tehran, Iran

ABSTRACT

The improvement of H-ZSM-5 catalyst for NO removal from stack of nitric acid unit was studied in this research. Selective catalytic reduction of NO was investigated on Pd, Ag, Cu and Ni impregnated on ZSM-5 in the presence of excess of oxygen. The new prepared catalysts were characterized by XRD, FTIR, H_2-TPR and N_2 adsorption-desorption methods. Successively, NO conversion increased with the reaction temperature transmission through a maximum, and then decreased at higher temperatures, because of the combustion of the ammonia on Pd/ ZSM-5and Cu/ ZSM-5 catalysts. The apparent activation energies in NO removal reaction have been determined for the prepared catalysts and it changes from 23 to 48 kJ/mol. In synthesis catalysts, partial dealumination were confirmed by XRD results. The results exhibited that the Cu/ZSM-5 and Pd/ZSM-5 catalysts had acceptable activity between 200 to 400 °C and under 250°C, respectively. It is found that the NO_x removal efficiency does not obey from the same pattern by rising temperature in all of these catalysts.

Keywords: ZSM-5; Selective catalytic reduction; Nitrogen oxides; cation effect

I. INTRODUCTION

Anthropogenic nitrogen oxides (NO_x, as NO and NO_2), mainly emitted from stationary and mobile combustion sources, are hazard for the environment and human health [1]. By the pioneering works [2], it has been well established that iron zeolites are among the most active catalysts for the selective catalytic reduction of nitrogen oxides by ammonia.

Noble metals or metal oxides (such as, MoO_3, CuO, Fe_2O_3, MnO_2, NiO, and V_2O_5) supported on suitable components have excellent catalytic activity for the selective reduction of NO to N_2 with NH_3 at relatively high reaction temperatures (greater than 250°C) [3-6]. Amongst these formulations, $V_2O_5/WO_3/TiO_2$ and Cu/HZSM-5 are available commercially [7]. The catalytic activity of some different ion exchanged zeolite such as doped- chabzite and MFI were reported by the other authors and imply that aluminosilicates are good supports for these types of catalysts [8].

Despite of the great number of references in literature, few detailed studies dealing to the comparison of the catalytic activity for the SCR of NO of different catalysts have been reported.

The present study was undertaken with aim of assessing the effect of four different transition metal chlorides and their reduction properties on activity of M/ZSM-5 zeolite (M= Ni, Pd, Ag, Cu) in ammonia selective catalytic reduction of NO to N_2. The ZSM-5 zeolite was impregnated with transition metal chloride in constant concentration of M/Al. The catalysts characterized after preparation by different method. In the new approach, the apparent activation energies and conversion in NO removal reaction have been determined for the prepared catalysts.

II. METHODS AND MATERIAL

18.33 gr of the commercial ZSM-5 zeolite (Si/Al=20) was added to an aqueous solution of 7.2 mmol of metal

chloride (Ni, Pd, Ag, Cu) under vigorous magnetic stirring and homogenized for 3 hours then ultrasonic treatment did for 45 min. The obtained solid samples were dried at 100 °C for 8 h and subsequently calcined at 480 °C for 3h. This method allows controlling the desired amount of metal ions in the zeolite. The chemicals were purchased from Merck Company.

The catalysts were characterized by various techniques: X-ray powder diffraction (Philips diffractometer with Cu-Kα radiation), temperature programmed reduction (Belcat A instrument), N_2 adsorption-desorption (Quantachrome corporation NOVA 2200) and FTIR spectroscopy (Bruker vertex 80).

The SCR activity measurements were conducted in an Inconel-800 fixed bed reactor (i.d. 15 mm) using 4 g of the catalyst with feed gas composition of 700 ppm NO; 500 ppm NH_3, 2.6 % O_2 and N_2 balance gas. The space velocity was 20000 h^{-1}. The conversion of NO was measured as a function of time and the concentration of O_2, NO and NO_2 were measured by gas analyser (Testo 340). The mass reaction rate of NO consumption and activation energy was calculated [9].

III. RESULTS AND DISCUSSION

A. Catalytic activity measurement

Figure 1 illustrates the temperature dependence of catalytic activity acquired in nitric oxide selective catalytic reaction with NH_3 for M/ZSM-5 samples. With raising reaction temperature in Cu/ZSM-5 activity increase and the NO conversion meets a maximum about 99.8% at 250°C and then it slowly decreases until 90% at 450°C. The performance of Pd/ZSM-5 catalyst passes a through maximum at 200°C because it involves competition ammonia oxidation at higher temperature. The catalyst with palladium is fit for low temperature and Ni/ZSM-5 and Ag/ZSM-5 exhibit acceptable activity in high temperature.

According to the literature [10], the SCR reaction is not dependent of the oxygen and ammonia concentration and is also first order with regard to the concentration of NO under the reactor testing conditions. Consequently, the first order rate constant can be estimated from NO conversion (X) by

$$K=V \ln(1-X)/m$$

Where V is the gas flow at the reaction temperature and m is the catalyst weight in grams. An approximation of the activation energy in agreement with K= A. EXP (-E_{act}/RT) was lead the Arrhenius plots were procured in 250 to 350°C range by calculating the rate of NO conversion data. The activation energy estimated from the regression lines are 35.9, 48, 23.2 and 25.0 kJ/mol for Cu/ZSM-5, Ni/ZSM-5, Pd/ZSM-5 and Ag/ZSM-5, respectively.
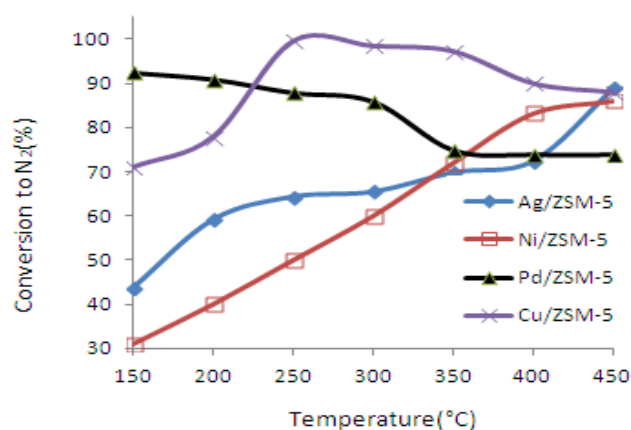

Figure 1: NO conversion efficiency of M/ZSM-5 (M= Cu, Pd, Ni)

B. Structural properties –XRD and FTIR spectroscopy

The powder X-ray diffraction was managed to determine the crystalline structure, lattice parameter and crystallinity of the catalysts. Fig. 1 exhibits the XRD patterns of all prepared catalysts after calcination. All catalysts were characterized by typical peaks at 7.92, 8.84, 23.12 and 23.8° in the XRD pattern of samples (JCPDS card NO: 049-0657) corresponding to the characteristic MFI structure peaks of zeolites, respectively. Copper oxides are not detectable by XRD technique, which implies that they are highly dispersed on the ZSM-5 carrier [11-12]. Besides the pattern of the Ni /ZSM-5, Pd / ZSM-5 and Ag / ZSM-5 illustrated nickel oxide (2θ=43.9°), palladinite(2θ=43.9°) and chlorargyrite(2θ=32.4, 46.4 and 28.0°) phases, respectively. The orthorhombic cell parameters of the ZSM-5 phase for these catalysts were calculated and results (table 1) showed small change in unit cell volume of them.
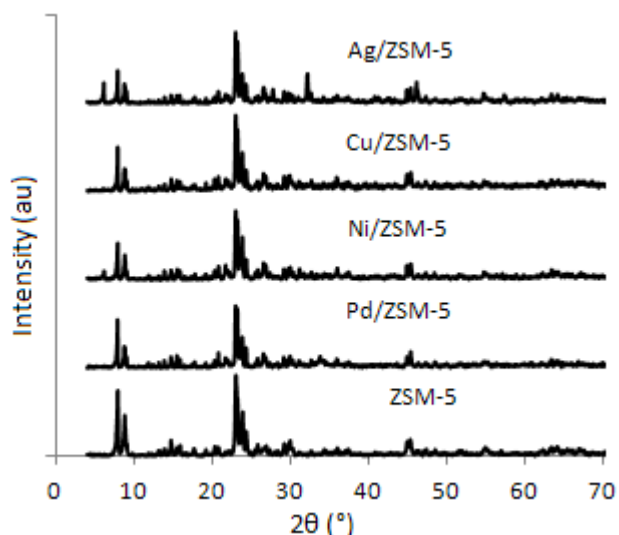
Figure 2: XRD pattern of samples

These results offer that the major amount of framework aluminum remained intact even after the impregnation and thermal treatment.

TABLE 1
LATTICE PARAMETERS OF M/ZSM-5 CATALYSTS

samples	Lattice parameter			volume
	a	b	c	$\mathring{A}^3$
Cu/ZSM	20.07	19.3615	13.4901	5242.05
Ni/ZSM	20.036	19.3473	13.5637	5257.858
Ag/ZSM	20.08	19.37315	13.4870	5246.63
Pd/ZSM	20.104	19.3666	13.5428	5272.82
ZSM-5	20.092	19.3498	13.4468	5227.78

According to table 2, it can be observed that all of samples indicate a relative crystallinity higher than 77%; therefore, the position of the peaks between 2θ=22-25° are slightly effected by framework dealumination.

TABLE 2I
STRUCTURE PROPERTIES FROM XRD

samples	Crystal size (nm)	Relative Cryst. (%)	Micro-stress (%)
Cu/ZSM	37.6	96.4	0.47
Ni/ZSM	67.5	81.7	0.5
Ag/ZSM	42.1	77	0.64
Pd/ZSM	58.4	94.2	0.36
ZSM-5		90	

Fig.3 shows FT-IR spectra of as-synthesized samples obtained by using different transition metals. The characteristic bands of five member ring of pentasil structure near 1220 and 546 cm^{-1} were observed in the all catalysts. The band at 790 cm^{-1} allocated of the symmetric stretching of the external linkage and 450cm^{-1} characteristic of T-O bending vibration of the SiO_4 and AlO_4 internal tetrahedral are present for the samples. [25]. In these spectra, an increase in the absorption band 1100 cm^{-1} related to the internal asymmetric stretching vibration of Si-O-T bonds was observed with doped transition metal ions, resulting the dealumination of HZSM-5. The broadening in the stretching vibrations of catalysts shows more band overlap relative to those of the M/ ZSM-5 catalysts. Hence, M/ ZSM-5 have a more heterogeneous surface than the ZSM-5 catalysts [13]. After reaction, the bands about 1450, 1657 and 1664cm^{-1} are attributing to the adsorbed ammonia species appeared for Cu/ ZSM-5 and Ni/ ZSM-5 catalysts. After the reaction termination, bi-dentate nitrates (1580 and 1525 cm^{-1}) adsorbed on Ni/ ZSM-5 was still present on the surface. It indicates that bi-dentate nitrate cannot easily react with ammonia to form H_2O and N_2; therefore, Ni/ ZSM-5 probably show lower activity to N_2 in NH$_3$-SCR.
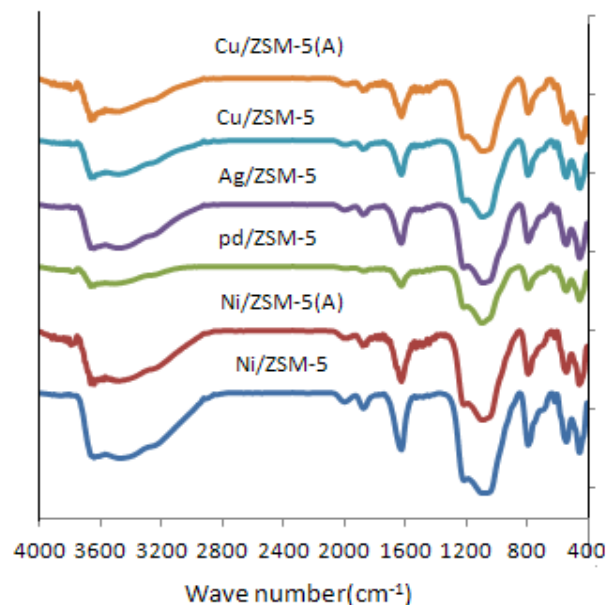

Figure 3: FTIR spectra of samples

The determined FAL (framework aluminum) contents of the catalysts were correlated to the symmetric stretching of the external linkage in the tetrahedral structural at ≈790-802 cm^{-1}. Triantafillidis and et al.[14] proposed the follow equation for an approximate calculation of FAL content per gram of samples:

$$Q_{FAL}= (802.5-\nu_2)/9.75$$

Where Q_{FAL} is the FAL content (in mg-atoms per gram hydrated catalyst) and ν_2 is the frequency of main symmetric stretching vibrations of FTIR spectra. Q_{TAL} (total content Al for the samples was determined by XRF ($\approx$ 0.76-0.83). The difference between the values of Q_{TAl} and Q_{FAl} gives EFAL content of the samples. The contents of extra-framework Si- and Al expressed as %SiO_2 and %Al_2O_3 and the Si/Al ratio of the extra framework/amorphous phases. Regards to table 3, an amount of amorphous material was present in these samples which principally included of Si species. The Si/Al ratio of the framework phases of these catalysts altered between 21.7 for ZSM-5 to 25.8 for Pd/ZSM-5.

TABLE 3
COMPOSITIONAL AND STRUCTURAL PROPERTIES OF THE CATALYSTS(XRF AND FTIR)

Sample	ν_2	Q_{FAL} (mg-atomsg^{-1})	Si/Al(fr)	SiO_2 (wt %) Amorphous
ZSM-5	796.6	0.61	21.7	8.94
Ni/ZSM-5	798.0	0.46	25.7	16.4
Cu/ZSM-5	796.2	0.64	22.2	2.7
Pd/ZSM-5	797.2	0.54	25.8	4.34
Ag/ZSM-5	797.5	0.51	21.8	21.4

C. Temperature-Programmed Reduction (TPR)

The TPR profiles of the catalysts are shown in Fig. 4. In general, the broad feature peaks in these samples may be related to the reduction of the reducible species on surface or inside the different cages of ZSM-5 zeolite. Similar to literature [17] the Cu/ZSM-5 samples showed two reduction regions. The first reduction was shown a sharp peak at 189 °C with a shoulder at 211°C ascribed to the bulk like CuO phase including large clusters of CuO. The second relatively broad peak with maximum at 315 °C assign to the highly dispersed copper species interacted strongly with ZSM-5 zeolite. The Cu/ ZSM-5 sample showed some broad peaks which implied the copper cations capture in the different sites in the zeolite. In The TPR profile of Ni/ ZSM-5 catalyst showed two overlapping peaks at centred 376 and 494 °C for bulk NiO and high dispersed nickel oxide in different sites of ZSM-5 zeolite, respectively [18].

Small peak in Ag/ ZSM-5 samples around 140°C attributed to the Ag_2O reduction and the peak at 335°C probably belong to silver silicates or silver aluminates species.

According to the literature [19], the reduction profile of PdO is attributed by a single peak at 55°C. Two reduction profiles are observed for the Pd/ZSM-5 catalysts. The first TPR peak temperature of Pd/ZSM-5 catalyst is at 55°C and the second peak is higher than that of PdO. This assigns that ZSM-5 inhibits the reduction partial of PdO. Easy reduction in M /ZSM-5 promotes NO removal. High dispersions of metal ions on ZSM-5 zeolite promote intimate contact between metal ions and surface.
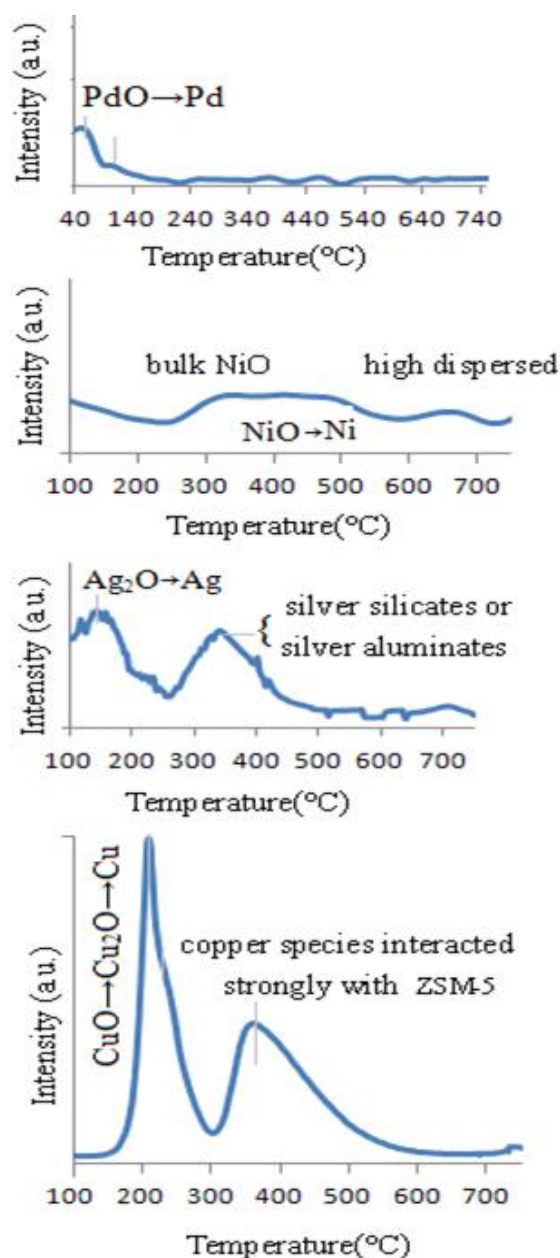
**Figure 4:** Temperature reduction profile of samples

M-O-(Si or Al) bonding forming is related to M-O-M bonding prevailing. The new bond formation between impregnated metal ions and Si or Al in zeolite framework is confirmed by changes in the location of reduction peaks in comparing by their bulk oxides. The presence of Si or Al in the coordination sphere of M^{n+} should change the electronic density and reducibility of metal ions in the catalyst.

The results showed that the activated phase in Ag/ ZSM-5 and Pd/ ZSM-5 may be a noble metal.

D. Textural and structure Properties

The isotherms of nitrogen adsorption- desorption (Fig.5) on the whole samples are similar to type I [20]. According to table 4, the meso-pore area of M /ZSM-5 (M=Ni, Cu, Pd) became larger than the parent ZSM-5. It was also proved that the meso-pores were generated during the modification process. Total surface area of these catalysts usually decreased between 7 to 16% after reaction. The shape of hysteresis loop signalizes the presence of inkstand-like pores in the catalysts.
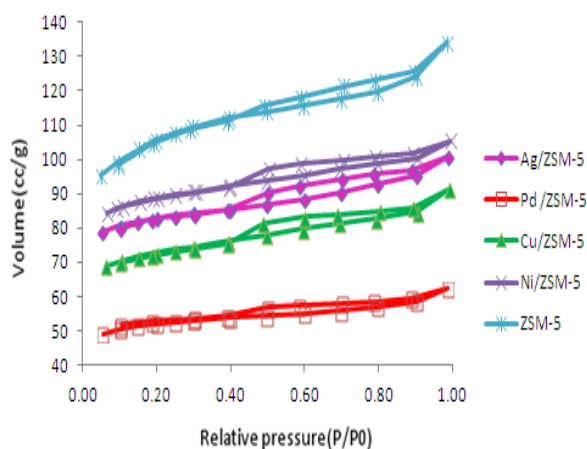
Figure 5: Adsorption/desorption isotherms of nitrogen on the samples

TABLE 4: SORPTION PROPERTIES OF THE M/ZSM-5 CATALYSTS

component	S_{BET} (m^2/g)	S_{ext} (m^2/g)	$V_{\mu p}$* (cm^3/g)	$S_{\mu p}$ (m^2/g)
Ni/ZSM-5	233	20	0.10	213
Cu/ZSM-5	223	31	0.09	192
Pd/ZSM-5	264	21	0.12	244
Pd/ZSM-5-A	245	23	0.11	222
Ag/ZSM-5	168	12	0.08	156
Cu/ZSM-5	279	23	0.12	256
Ni/ZSM-5	291	28	0.13	263
ZSM-5	348	34	0.17	314
A: After reactor			μp: Micro Pore	

IV. CONCLUSION

Impregnation by metal chloride partially caused dealuminated ZSM-5 zeolite. Among the catalysts prepared in this study Cu/ZSM-5 illustrated high performance in the all reaction temperature range. At the 360 °C, temperature supplied necessary activation energy for starting reaction for all of the catalysts; therefore, we did not observe strongly effect of variety of apparent activation energy in the performance of catalysts. The cell volume of ZSM-5 in these catalysts increased in comparing to parent ZSM-5. The redox properties play more important role than acidic properties in this reaction. To regard of our knowledge the reduction of bulk metal oxide usually starts at a lower temperature than M/ZSM-5 catalysts in this research. Furthermore, the higher reduction temperature of supported metal ions showed a strong interaction between metal and support. The rate-determining step in the SCR reaction may be the same for M/ ZSM-5 (M= Ni, Cu), while it appeared to be different for the Pd/ ZSM-5 and Ag/ ZSM-5. The first group is metal oxide in the reaction condition and the second group is metal state, therefore, shows lower apparent activation energy.

VI. REFERENCES

[1] Z. Zhang, J. D. Atkinson, B. Jiang, M. J. Rooda and Z. Yan (2015) Appl. Catal. B, Vol. 163, pp 573–583.

[2] P. Sazama, B. Wichterlova, E. Tabor, P. Šťastnyˊ , N. K. Sathu, Z. Sobalik, J.Devˇdecˇek, Š. Sklenak, P. Klein, A. Vondrova (2014) J. Catal. , Vol. 312, pp 123–138.

[3] G. Yan, LUAN Tao, LÜ Tao, C. Kai, X, Hongming (2013) Chin. J. Chem. Eng. Vol 21(1), pp 1-7.

[4] N. Apostolescu, T. Schröder, S. Kureti,(2004) Appl. Catal. B, Vol. 51, pp 43–50.

[5] I. Nova, L. Castoldi, L. Lietti, E. Tronconi, P. Forzatti, F. Prinetto, G. Ghiotti, (2004) J. Catal., Vol. 222, pp 377–388.

[6] J. Despres, M. Koebel, O. Kröcher, M. Elsener, A. Wokaun, (2003) Appl.Catal. B, Vol. 43, pp 389–395.

[7] D. Y. Yoon, E. Lim, Y. J. Kim, J. H. Kim, T. Ryu , S. Lee, B. K. Cho ,I. Nam , J. W. Choung, S. Yoo, (2014) J. Catal. , Vol. 319, pp 182- 193.

[8] J. A. Loiland, R. F. Lobo, (2014) J. Catal. Vol. 311, pp 412–423.

[9] S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff , (2010) Appl. Catal. B, Vol. 95, pp 348–357.

[10] S. Brandenberger, O. Kröcher, M. Casapu, A.Tissler, R. Althoff, (2011) Appl. Catal. B Vol. 101, pp 649-659.

[11] Q.H. Trinh, S.B. Lee, Y.S. Mok (2015) J. Hazard. Mater. Vol.285 pp.525.

[12] R. López-Fonseca, B. de Rivas, J.I. Gutiérrez-Ortiz, A. Aranzabal, J.R. González-Velasco (2003) Appl. Catal. B: Vol. 41 pp 31–42.

[13] A. Savara, A. Danon, W.M.H. Sachtler, E. Weitz, (2009) Phys. Chem. Chem. Phys, Vol. 11 pp 1180–1188.

[14] C. S. Triantafillidis, A.G. Vlessidis, L. Nalbandian, N. P. Evmiridis(2001) Micropor. Mesopor. Mat., *Vol.* 47, *pp* 369-388.

[15] J. M. Campos-Martín, A. Guerrero-Ruiz, J. L. G. Fierro(1996) Catal. Lett., *Vol.*41(1-2), *pp* 55-61.

[16] Ch. Li, Y.Chen (1995)Thermochim. Acta, Vol. 256 pp 457 - 465.

[17] L. Chmielarz, A. Wegrzyn, M. Wojciechowska, S. Witkowski, M. Michalik (2011) Catal. Lett., Vol. 141, pp 1345–1354.

[18] H. Y. Lin, Y. W. Chen (2004) Mater. Chem. Phys., Vol. 85, pp 171–175.

[19] Meng-Fei Luo, Zhao-Yin Hou, Xian-Xin Yuan and Xiao-Ming Zheng (1998) Catal. Let. Vol. 50 , pp 205-209.

[20] Webb, P. A.; Orr, C.(1997)Analytical Methods in Fine Particle Technology; Micromeritics,.