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Ag-modified H-Beta, H-MCM-41 and SiO_2: Influence of support, acidity and Ag content in ozone decomposition at ambient temperature

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Abstract

Silver-modified H-MCM-41-50, H-Beta-11 and SiO_2 catalysts were synthesized by incipient wet impregnation method using aqueous solution of silver nitrate. The catalysts were characterized using X-ray powder diffraction, scanning electron microscope, X-ray fluorescence, nitrogen physisorption and FTIR spectroscopy. The catalysts were tested in the heterogeneous catalytic decomposition of ozone at ambient temperature. The highest degree of ozone decomposition was observed over the mild acidic 5 wt.% Ag-H-MCM-41-50 (98%) mesoporous molecular sieve catalyst followed by 5 wt.% Ag-SiO_2 (90%). It was found that the most acidic catalyst 5 wt.% Ag-H-Beta-11 showed the lowest ozone decomposition. The content of Ag was also observed to influence the ozone decomposition. The 5 wt.% Ag-H-MCM-41-50 mesoporous molecular sieve catalyst exhibited higher catalytic activity than 2 wt.% Ag-H-MCM-41-50. The acidic properties, structure of catalyst supports and the metal content were found to be important for the ozone decomposition reaction.

Keywords: Ozone decomposition; MCM-41; Silver; Zeolite; Mesoporous materials

1. Introduction

Ozone is harmful for health, living organism and human environment. Enhancement of ozone level in big cities increases cardiovascular and respiratory problems. Furthermore, ozone may cause inflammation of lungs and increase in frequency of asthma attacks. It is also one of the reasons for urban smog. The formation of ozone can take place by interaction of sunlight with the emissions from cars and power plants [1]. Hence, the catalytic decomposition of ozone is an important area of research from environmental and health point of view.

Ozone treatment is a widely used method for purification and sterilization of waste and natural waters, as well as oxidation of organic substances. As a result of oxidation the waste gases contain residual concentration of ozone, which is above the admissible values, and it must be decomposed. Ozone decomposition has been reported over metal oxide catalysts [2–6]. However, there are only a few investigations reported in the literature regarding ozone decomposition over Ag-modified zeolite, silica and mesoporous molecular sieve catalysts [7,8]. In this work, we report ozone decomposition over Ag-modified H-MCM-41-50, H-Beta-11 and SiO_2 catalysts. Beta zeolite is a microporous material and consists of three-dimensional interconnected 12 MR channel systems. Two morphologically identical linear channel systems have pore openings of 7.5 Å × 5.7 Å and the third channel system with pore openings 6.5 Å × 5.6 Å is non-linear [9]. Na-MCM-41 is a partially crystalline mesoporous molecular sieve with hexagonal shape pores and uniform channel systems. The pore size of MCM-41 can be varied from 20 to 100 Å and has very high surface area [10]. The aim of the present work is to investigate the influence

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of support acidity and structure of zeolite and mesoporous molecular sieve in the heterogeneous catalytic decomposition of ozone. Furthermore, the influence of Ag-loading in MCM-41 and modification of Ag-H-MCM-41 with Ce was also studied for the decomposition of ozone.

2. Experimental

2.1. Catalysts synthesis

The Na-MCM-41-50 mesoporous molecular sieve and Na-Beta-11 zeolite were synthesized in a 300 ml autoclave using methods as mentioned in Refs. [11,12] with some modifications. After completion of synthesis of Na-MCM-41-50 and Na-Beta-11, the materials were filtered, washed thoroughly with distilled water, dried at 383 K and calcined at 823 K in a muffle oven to remove the organic template. The Na-MCM-41-50 mesoporous molecular sieve and Na-Beta-11 zeolite were ion-exchanged with ammonium chloride, washed with distilled water dried at 383 K and calcined at 773 K in a muffle oven to proton forms of H-MCM-41-50 and H-Beta-11. SiO_2 was delivered commercially from Merck Company. Five weight percent Ag-modified H-MCM-41-50, H-Beta-11, SiO_2 and 2 wt.% Ag-Ce-H-MCM-41-50 catalysts were prepared using incipient wet impregnation method in a rotator evaporator device at room temperature. Aqueous solution of silver nitrate was used as a precursor for Ag. Introduction of the Ce was done by ion-exchange (IE) of the proton form using Ce-nitrate solution followed by filteration, washing with distilled water, drying at 383 K and calcination at 773 K.

2.2. Catalysts characterization

The specific surface area of the supported catalysts was determined by nitrogen adsorption using Sorptomatic 1900 (Carlo Erba Instruments). The Dubinin equation was used for calculation the surface area of the zeolite and the B.E.T. equation for the mesoporous molecular sieve and silica. To verify the crystal structure of the synthesized zeolites, X-ray powder diffraction measurements was applied on a Bragg–Brentano $\theta/2\theta$ reflection geometry based Philips PW1820 diffractometer using Cu Kα ($\lambda = 1.54184$ Å) radiation. The Cu X-ray tube voltage was set to 40 kV and the current to 50 mA. The divergence of the primary X-ray beam was limited by an automatic divergence slit (ADS) and a 15 mm mask. The irradiated sample length was set at a fixed 12 mm. On the diffracted side there was a 0.2 mm receiving slit and a 1° anti-scatter slit. The diffracted X-ray beam was filtered with a Ni Kβ filter. The measured diffractograms were analyzed using X'Pert HighScore software (Philips, 2001) and the powder diffraction file (PDF) database (PDF-2, sets 1-46, 1996 release, ICDD). The PDF database was used to identify the sample peaks and the corresponding phases. The crystal morphology of the samples was studied using a scanning electron microscope (Cambridge Leica 360). The Si/Al ratio of Na-MCM-41 and Na-Beta was determined by X-ray fluorescence. The metal content of the samples was determined by the inductively coupled plasma atomic emission spectrometry (ICP–AES) with a Jobin Yvon 38, France. The FTIR spectra were recorded on Fourier transformed infrared spectrometer (ATI Mattson) using pyridine as a probe molecule.

2.3. Catalytic experiments

The catalytic activity and long-term stability towards heterogeneous decomposition of ozone were investigated in an isothermal plug flow reactor under steady state conditions without temperature gradients. The catalyst particle size (0.2–0.4 mm) was chosen taking into account the reactor diameter (4.0 mm) and the volume rate (mean value 133,333 h^{-1}, calculated on the total catalyst bed volume) in order to reduce the effect of external diffusion. Pre-treatment of the catalysts included heating at 110 °C for 1.5 h in air flow. The rate of the gas flow was 5.6 l/h and the catalyst volume, 0.042 cm^3.

Ozone was synthesized in a flow of oxygen (99.7%) dried with silica gel using ozone generator with a silent discharge of 4–6 kV between the electrodes. The inlet concentration of ozone was 4390 ppm. Ozone concentration was analyzed with an Ozomat GM (Anseros, Germany) analyzer with an accuracy of ±50 ppm. The carrier gas was oxygen. The reaction temperature was ambient (23 °C) and was maintained with an accuracy of ±0.2 °C. The activity of the catalysts was measured after 15 min and was calculated on the basis of equations:

$$\text{Conversion}\,[\%] = 100 \times \left[\frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}}\right];$$

$$\text{Rate constant}\,[\text{h}^{-1}] = -\text{GHSV} \times \ln\left[1 - \frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}}\right],$$

where C_{inlet} and C_{outlet} are the ozone concentrations in inlet and outlet of the reactor. The detail description of catalysts testing in ozone can be found in Ref. [13].

3. Results and discussion

3.1. Catalyst synthesis and characterization results

The X-ray powder diffraction patterns and scanning electron micrographs of 5 and 2 wt.% Ag-H-MCM-41-50, 5 wt.% Ag-H-Beta-11 and 2 wt.% Ag-Ce-H-MCM-41-50 catalysts showed that the structure and morphology were those of Beta and MCM-41. The X-ray powder diffraction patterns of 5 wt.% Ag-H-MCM-41-50 and 5 wt.% Ag-SiO_2 catalysts are given

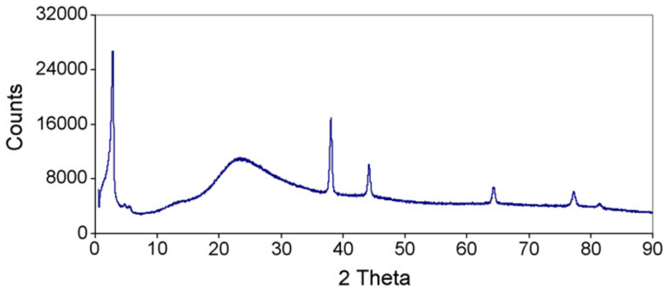

Fig. 1. X-ray powder diffraction pattern of 5 wt.% Ag-H-MCM-41–50.

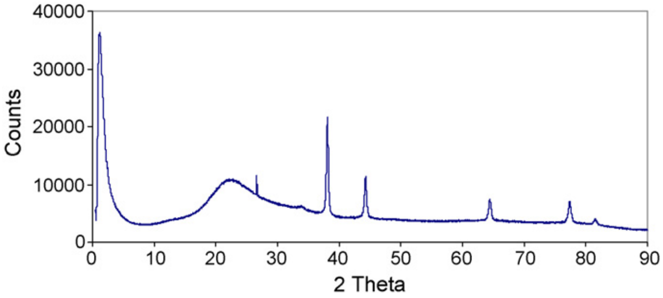

Fig. 2. X-ray powder diffraction pattern of 5 wt.% Ag-SiO$_2$.

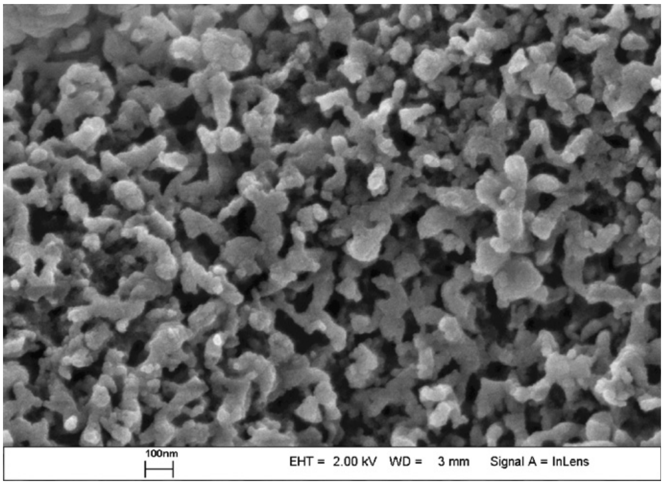

Fig. 3. Scanning electron micrograph of 5 wt.% Ag-H-MCM-41-50.

in Figs. 1 and 2, respectively. The major Ag peaks in 5 wt.% Ag-SiO$_2$ were identified at 2θ values of 38.1°, 44.3°, 64.4° and 78°. The average crystallite size of Ag in 5 wt.% Ag-SiO$_2$ and 5 wt.% Ag-H-MCM-41-50 was measured to be 39.1 and 33.3 nm, respectively.

The SEM micrograph of 5 wt.% Ag-H-MCM-41-50 catalyst is given in Fig. 3. The XRD patterns and SEM micrographs clearly showed that the MCM-41 and Beta zeolite kept their structures intact even after H- and Ag- and Ce-modifications.

The acidic properties of H-Beta-11, H-MCM-41 and SiO$_2$ catalytic materials were investigated by FTIR using pyridine as a probe molecule [14,15]. The FTIR investigation reveals that the H-Beta-11 microporous zeolite is the most acidic support from the three studied catalytic support materials. The H-MCM-41 mesoporous molecular sieve was the second most acidic support and SiO$_2$ was the least acidic. The acidity of the three catalytic supports decreased in order of H-Beta-11 > H-MCM-41 > SiO$_2$. The Si/Al ratios of MCM-41 and Beta zeolite were determined to be 50 and 11, respectively.

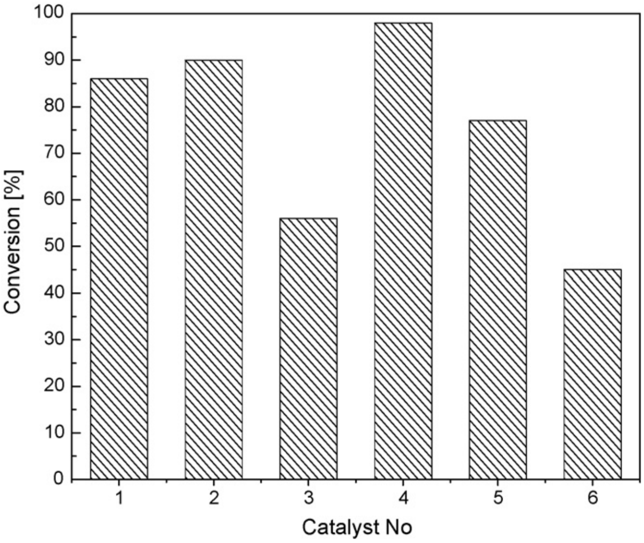

Fig. 4. Degree of ozone decomposition at room temperature over different silver modified supported catalysts. The numbers of the catalysts correspond to Table 1.

The specific surface area, the total pore volume and the masses of the supported catalysts are presented in Table 1. As can be seen, the 2 wt.% Ag-H-MCM-41-50 mesoporous molecular sieve catalyst showed the highest surface area of 886 m^2/g followed by 2 wt.% Ag-Ce-H-MCM-41-50 (823 m^2/g) and 5 wt.% Ag-H-MCM-41-50 (723 m^2/g). The reason for decreasing the surface area is due to an additional amount of Ce in the second catalyst and to a higher loading of Ag in the third one. However, surface areas of all mesoporous molecular sieve catalysts are higher than that of the 5 wt.% Ag-H-Beta-11 microporous zeolite catalyst. The lowest surface area was obtained for silver modified silica catalysts.

3.2. Ozone decomposition

Fig. 4 presents the degree of heterogeneous decomposition of ozone over the different silver modified supported catalysts at ambient temperature. As can be seen the highest decomposition of ozone was observed over the mild acidic catalyst 5 wt.% Ag-H-MCM-41-50 mesoporous molecular sieve. The most acidic catalyst 5 wt.% Ag-H-Beta-11, i.e. with the lowest

Table 1
Total pore volumes, surface areas, masses and rate constants of the prepared catalysts

No.	Catalysts	Total pore volume [cm^3/g]	Surface area [m^2/g]	Mass [g]	Rate constant [$\times 10^5$ h^{-1}]
1	2 wt.% Ag/SiO$_2$	0.99	323	0.0281	2.62
2	5 wt.% Ag/SiO$_2$	1.04	342	0.0276	3.07
3	2 wt.% Ag-H-MCM-41–50	1.23	886	0.0372	1.09
4	5 wt.% Ag-H-MCM-41–50	1.12	723	0.0358	5.22
5	2 wt.% Ag-Ce-MCM-41–50	1.14	823	0.0475	1.96
6	5 wt.% Ag-H-Beta-11	0.20	574	0.0382	0.80

Si/Al ratio, showed the lowest ozone decomposition degree (Fig. 4), unequivocally indicating the role of support acidity in the reaction of ozone decomposition. The characterization of H-Beta-11 zeolite for its acidic property by FTIR showed that it was the most acidic catalytic material out of the three investigated supports. The 5 wt.% Ag-SiO_2 catalyst exhibited second highest ozone decomposition further indicating that the mild acidic supports such as H-MCM-41 and SiO_2 are preferred for this reaction. The investigation of the acidic properties by FTIR showed that both the H-MCM-41-50 and SiO_2 supports were mild acidic. Hence, with increase of the Si/Al ratio, i.e. decrease of the catalyst acidity, the degree of heterogeneous catalytic decomposition of ozone become higher. Therefore, the 5 wt.% Ag supported on H-MCM-41-50 and SiO_2 catalysts showed very high conversion for reaction of ozone decomposition, whereas H-Beta-11 which is highly acidic zeolite, exhibited low degree of ozone decomposition. The ozone decomposition was lower (49.5%) in more acidic 2 wt.% Ag-H-MCM-41-20 than less acidic 2 wt.% Ag-H-MCM-41-50. The reason for the higher ozone decomposition over lower acidic catalysts can be due to larger formation of oxygen species intermediate such as ozonide ion (O_3^-) and oxygen ion (O^-). One of the reasons for the larger formation of ozonide (O_3^-) and oxygen ion (O^-) and there by increasing the ozone decomposition could be enhancement of absorption property of ozone over weak acid sites.

The time–conversion dependence measured for 390 min over the most active catalysts is given in Fig. 5. One can see that the conversion is stable and almost constant with time on stream at room temperature. The rate constants of all catalysts are presented in Table 1.

It was observed that the acidity was not the only factor influencing the degree of ozone decomposition, structure of the catalytic materials also observed to play a significant role. The H-Beta-11 zeolite is a microporous with well-defined pore size and regular channel systems. The H-MCM-41 is a mesoporous molecular sieve containing hexagonal uniform channels with framework Al and silica is a mesoporous material with non-uniform pores. The reason for a better conversion in reaction of ozone decomposition over 5 wt.% Ag-H-MCM-41-50 catalyst than over 5 wt.% Ag-SiO_2 can be explained from one hand to a higher surface area of H-MCM-41-50 catalysts and for another to an uniform hexagonal channel system with framework Al in the structure.

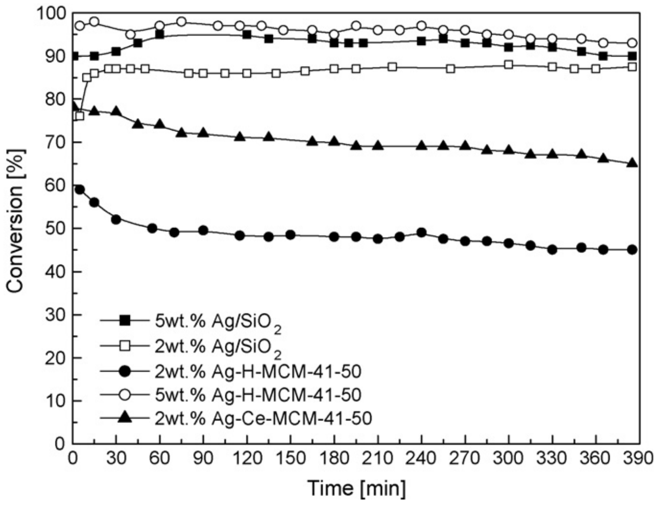

Fig. 5. Long-term stability test in reaction of ozone decomposition at room temperature over different silver modified catalysts.

The higher activity of 5 wt.% Ag-modified H-MCM-41-50 and SiO_2 in comparison with 2 wt.% on the same supports (Fig. 5) clearly indicates that besides acidity and structure of the supports, the content of Ag is very significant for this reaction. With increase in the silver loading the activity of the catalysts become higher.

It is interesting, that among 5 wt.% silver-containing samples the most active is 5 wt.% Ag-H-MCM-41-50 catalyst, but among 2 wt.% silver-containing samples the most active is 2 wt.% Ag-SiO_2 (see Table 1). One possible explanation of this behavior is given as follows. The silver can be present on the carrier surface in the form of both: isolated ions and clusters. At low metal content isolated silver ions pre-dominate, which are less active in ozone decomposition. The formation of the more active clusters begins when the carrier surface is ‘‘saturated’’ with silver ions. The amount of clusters formed on H-MCM-41 at low silver content is less, because of its higher surface area in comparison with that of SiO_2. At higher silver content (5%), the higher surface area of H-MCM-41 is an advantage, because the carrier gives more surface area for cluster formation. On other hand, the small increase of the catalytic activity of 5 wt.% Ag/SiO_2 in comparison with 2 wt.% Ag/SiO_2 (see Table 1) is an indication that on SiO_2 proceeds agglomeration at higher metal loadings. Based on crystallite size measurement data of 33.3 and 39.1 nm for of 5 wt.% Ag-H-MCM-41-50 and 5 wt.% Ag-SiO_2, respectively, it was inferred that lower crystallite size of Ag is favoured ozone decomposition.

The ozone decomposition activity is also enhanced by the addition of base metal Ce. The 2 wt.% Ag-Ce-H-MCM-41-50 shows higher conversion with almost 20% more than that of 2 wt.% Ag-H-MCM-41-50 catalyst. But even with this additional metal 2 wt.% Ag-Ce-H-MCM-41-50 exhibit lower conversion than that of the most active 5 wt.% Ag-H-MCM-41-50 catalyst, because of the lower silver loading. The presence of Ce in Ag-H-MCM-41-50 may have a stabilizing effect towards stability of the catalysts during the ozone decomposition reaction. However, the stabilizing effect of Ce needed to be investigated further.

4. Conclusions

Silver modified mesoporous molecular sieves, zeolite catalysts and silica were synthesized by incipient wet impregnation method, characterized by different techniques and tested in heterogeneous catalytic decomposition of ozone. Very high catalytic activity was observed at room temperature and at the same time the catalysts remains active with the time. The most active 5 wt.% Ag-H-MCM-41-50 catalyst exhibit almost 100% conversion at room temperature, followed by 5 wt.% Ag-SiO_2 (90%).

Three main factors were found to have an influence on the high catalytic activity in reaction of ozone decomposition: (i) choice of the support, giving the needed structure, surface area and acidity; (ii) silver loading; (iii) modifying the catalyst with more basic metal.

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References

[1] M.L. Bell, A. McDermott, S.L. Zeger, J. Am. Med. Assoc. 292 (2004) 2372.
[2] B. Dhandpadni, S. Oyama, Appl. Catal. B: Environ. 11 (1997) 129.
[3] D. Mehandjiev, A. Naydenov, G. Ivanov, Appl. Catal. A: Gen. 206 (2001) 13.
[4] A. Naydenov, D. Mehandjiev, Appl. Catal. 97 (1993) 17.
[5] Z. Hao, D. Cheng, Y. Guo, Y. Liang, Appl. Catal. B: Environ. 33 (2001) 217.
[6] C. Heising, W. Zhang, T. Oyama, Appl. Catal. B: Environ. 14 (1997) 117.
[7] N. Kumar, P. Konova, A. Naydenov, T. Heikillä, T. Salmi, D.Yu. Murzin, Catal. Lett. 98 (1) (2004) 57.
[8] S. Imamura, M. Ikebata, T. Ito, T. Ogita, Ind. Eng. Chem. Res. 30 (1991) 217.
[9] M. Treacy, J. Newsam, Nature 332 (1988) 249.
[10] S. Beck, US Patent 5,057,296 (1991).
[11] C. Kresge, M. Leonowicz, W. Roth, J. Vartuli, US Patent 5,098,684 (1992).
[12] R. Wadlinger, G. Kerr, E. Rosinski, US Patent 3,308,069 (1997).
[13] P. Konova, A. Naydenov, D. Mehandjiev, Bulg. Chem. Commun. 34 (2002) 437.
[14] P. Arvela, N. Kumar, V. Nieminen, R. Sjöholm, T. Salmi, D.Yu. Murzin, J. Catal. 225 (2004) 155.
[15] D. Kubicka, N. Kumar, P. Mäki-Arvela, M. Tiitta, V. Niemi, T. Salmi, D.Y. Murzin, J. Catal. 222 (2004) 65.