

MULTIFUNCTIONAL MECHANOCHEMICALLY-SYNTHESIZED Fe₂O₃-ZnO MIXED OXIDE

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ABSTRACT

Fe₂O₃-ZnO mixed oxide with 1% wt. Fe has been synthesized using the mechanochemical activation method. The catalytic properties of Fe₂O₃-ZnO mixed oxide as catalyst has been investigated using the decomposition of isopropanol as model reaction. The photocatalytic activity of the Fe₂O₃-ZnO mixed oxide, using ethylene as a model air pollutant, has been carried out in a gas-phase flat-bed continuous flow photocatalytic reactor. Ethylene conversion degree was taken as a measure of the photocatalytic activity of the sample. The performance of the Fe₂O₃-ZnO photocatalytic material is compared with the standard reference photocatalyst Degussa P25 (75% anatase TiO₂ + 25% rutile TiO₂).

Key words: *mixed oxides, mechanochemical synthesis, photocatalytic activity*

INTRODUCTION

Mixed oxides, which contain more than one kind of metal atom are important class of catalysts that are widely used in several fields of investigation related to catalysis [1–4]. ZnO and TiO₂ have been widely used as photocatalyst owing to their high activities, low costs and environment-friendly properties [5]. However, the photocatalytic activities of ZnO and TiO₂ are limited to irradiation wavelengths in the UV-region because of their wide band-gaps and they can absorb only UV light. Some problems still remain to be solved in their application, such as the fast recombination of photogenerated electron-hole pairs. Therefore, improving the photocatalytic activity by modification of the material has become a topic among researchers in recent years. One approach is to dope transition metals into ZnO [6–8]. Some of the recent publications on Fe-doped ZnO systems using different methods of sol–gel techniques have examined the influence of Fe doping on the nanostructures and optical properties [9, 10]. The mechanochemical method for preparation of mixed oxides becomes more widely used at present due to its relative simplicity and availability [11, 12].

The contamination of air with various volatile organic compounds, originating from the petrochemical industry, presents a serious environmental problem due to the intrinsic toxicity and stability of some of these compounds. The photocatalytic degradation of organic compounds using semiconductor particles, most often nanometer-sized transition metal oxides, represents a promising solution to this environmental problem. Ethylene or its chlorinated derivatives have often been selected as target pollutants in air by many researchers in view of the large-scale production in the petrochemical plants (ethylene is the most widely produced petrochemical) causing air pollution in such industrial sites. Ethylene emissions are of concern because its release can lead to the formation of extremely toxic oxides.

The purpose of this work was to investigate the multifunctional properties of the mechanochemically prepared Fe₂O₃-ZnO (1%wt. Fe) mixed oxide. Its acid-base properties were studied using isopropanol decomposition as catalytic test reaction. In the second case of air purification the mechanochemically prepared mixed oxide is applied as film coating on a support to oxidize photocatalytically ethylene as model pollutant in air.

EXPERIMENTAL

Mechanochemical synthesis of Fe₂O₃-ZnO mixed oxides was performed in a laboratory planetary mill Pulverisette 6 (Fritsch, Germany) by high-energy milling of hematite and ZnO. The following experimental conditions were applied for the mechanochemical synthesis: loading of the mill, 50 balls of 10 mm in diameter; material of milling chamber and balls was tungsten carbide; volume of milling chamber, 250 mL; room temperature; rotational speed of the mill planet carrier, 400 min⁻¹; milling time, 20 min.

X-ray powder diffraction patterns (XRD) of the samples were registered at room temperature with a TUR M62 apparatus with PC management and data accumulation, using HZG-4 goniometer with CoK_α radiation. The XRD lines were identified by comparing the measured patterns to the JCPDS data cards.

Catalytic performance of the samples was performed on a flow reactor-gas chromatography system under atmospheric pressure by using isopropanol decomposition as reaction probe. 0.2 g of catalyst was charged into the reactor. Argon was used carrier gas. Isopropanol was put in saturator. The temperature of saturator was kept at 273 K. The reactor was directly connected to a 2 m GC column filled with Chromosorb W (60–80 mesh) with 20 % Carbowax 400 at 313 K [13]. Isopropanol conversion to propene was used as a measure of acidity and that to acetone is a measure of basicity of the sample.

The measurement of the photocatalytic activity of material Fe₂O₃-ZnO has been carried out in a gas-phase flat-bed continuous flow POLITEF photocatalytic reactor, using ethylene as a model air pollutant. The course of the photocatalytic reaction of complete oxidation of ethylene was monitored by means of a gas-analyzer (LANCOM III, Land Instruments Co., England), equipped with a sensor for total hydrocarbon content in a gaseous mixture (ppm C_xH_y). The inlet mixture is fed into the reactor by a 4-channel mass flow regulator (Matheson Model 8249), having the following composition: 10000 ppm C₂H₄, 10% O₂, 90% N₂. The nitrogen was fed into the reactor via two channels – the first channel feed N₂ directly into the reactor (dry N₂), while the second channel feeds the nitrogen flow to the water vapor saturator (distilled H₂O) to saturate the stream (moist N₂) and then further to the reactor. The use of two independently regulated channels for feeding nitrogen to the reactor enables the variation of the humidity of the inlet

gaseous mixture, which is a very important parameter of a photocatalytic process of oxidation.

During our previous experimental runs with other photocatalyst samples it was established that the optimal relative humidity RH is 30% [15].

Feeding ethylene and oxygen through two other independently regulated channels allows varying the ratio $C_2H_4 : O_2$ – in all our experimental runs the oxygen concentration is in large excess with respect to the amount of oxygen needed stoichiometrically to achieve 100% conversion degree of ethylene. So we can accept that at moderate conversion degrees the oxygen concentration C_{O_2} is practically unchanged comparing the inlet and the outlet compositions. In this specific case C_{O_2} is incorporated into the value of the effective kinetic constant k_{eff} in the kinetic equation:

$$R_{C_2H_4} = k_{\text{eff}} \cdot C_{C_2H_4} / (1 + K_{O_2} \cdot C_{O_2} + K_{C_2H_4} \cdot C_{C_2H_4}) \quad (1)$$

In the equation (1) $R_{C_2H_4}$ is the rate of consumption of ethylene (mol/h.g-cat), $C_{C_2H_4}$ is the concentration of ethylene at the outlet of the reactor (mol/cm³), while K_{O_2} and $K_{C_2H_4}$ are the adsorption-desorption equilibrium constants of oxygen and ethylene respectively. The equation (1) corresponds to a mechanism of the type of Langmuir-Hinshelwood, which means that both the reactants react on the surface of the photocatalyst in adsorbed state and there is no inhibiting effect by the reaction products – CO₂ and H₂O. This is often applied in the so called „formal kinetic approach“. The maximum contact time of ethylene τ_c under our experimental conditions is 4 min (such is the capacity of the experimental set-up i.e. the possibilities of the four-channel mass flow controller) – at this value of τ_c we achieve the maximum possible conversion degree of ethylene (if the relative humidity is also optimal and oxygen is in large excess). For avoiding under-pressure in the reactor and improving the precision of the analyses a GC flow splitter was used. It was placed between the reactor outlet and the gas-analyzer and the coefficient of dilution was measured to be 53.47 using CO₂ standard. The standard concentration of CO₂ in the cylinder was 19.25% and the gas-analyzer measured concentration 0.36% CO₂, on the basis of which the dilution coefficient was evaluated to be 53.47. Therefore the reading of the gas-analyzer for total hydrocarbons C_xH_y has to be multiplied by the coefficient to obtain the real concentration at the reactor inlet (the value measured in the dark) and at the reactor outlet (the value measured under irradiation).

1. Types of illumination and illumination intensity

a. UV-A light

The width of the flat rectangular quartz glass illumination window (the dimensions are: 5 cm x 15 cm x 0.5 cm) of the reactor enables the use of two linear lamps simultaneously (4-Watt UV-A lamps Philips model TL4W/08 F4T5/ BLB with total power of illumination 8 Watts, placed lying directly upon the window (distance 0 cm) – the intensity of illumination is 0.014 W/cm². This is polychromatic kind of illumination with wavelength range 320–400 nm and a maximum at 365 nm.

b. UV-C light

Two lamps Philips TUV 4W/G4 T5 (monochromatic light $\lambda = 254$ nm) of light power 4 Watts (making a total of 8 Watts), placed lying directly upon the window (distance 0 cm) – the intensity of illumination is the same – 0.014 W/cm², however this kind of illumination is a high frequency one i.e. the photons have much higher energy.

c. Visible light

This irradiation was accomplished using a linear halogen lamp Tungfram 500 Watts K1R7s giving intensity of illumination 8.9 mW/cm² (9700 Lm) at 50 cm from the surface of the illumination window. This kind of lamp causes considerable heating of the quartz window and reducing the distance of illumination could be risky in view of the inflammability of ethylene air mixtures. The other experimental conditions (the flow rates and the contact time) are the same as in the experiments with UV-light.

2. Deposition of thin film photocatalytic coating on TLC sheet

Merck aluminum foil, pre-coated with silica gel (0.2 mm) was used as support for the photocatalytic coating of the powder nano-sized material. It is available commercially and used for the purposes of thin layer chromatography (TLC Merck Art.5554 Kieselgel 60 F₂₅₄). The commercial sheet has dimensions 25 cm x 25 cm. A rectangular piece is easily cut out (4.2 cm x 13.4 cm) to fit with the dimensions of the accommodation nest drilled in the bed of the POLITEF photocatalytic reactor. The total geometric illuminated surface area amounts to 56 cm². An amount of 56 mg of the powder nanosized photocatalytic material is weighed exactly, in order to obtain a coating of 1mg/cm², in a weighing funnel. The amount was transferred quantitatively by rinsing it with de-ionized water in a volumetric

flask of 5 ml and filled up to the mark. The flask, containing the suspension (56 mg of $\text{Fe}_2\text{O}_3\text{-ZnO}$ in 5 ml H_2O), is immersed in a large beaker with water and fixed firmly in it, without touching the walls of the beaker. The sonotrode of an ultrasonic processor Hielscher UP 200S is also immersed in the water beaker. The ultra-sonic bath treatment (24 kHz) is carried out at maximal amplitude in continuous mode (cycle 1) to disintegrate the agglomerates for 1 hour. After the sonication the suspension is deposited on the TLC sheet uniformly using a directing air stream all over the surface. Then the film is dried with until a constant weight is obtained. The sample is ready for measuring the photocatalytic activity.

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of undoped ZnO as well as 1 % wt. Fe doped ZnO, respectively.

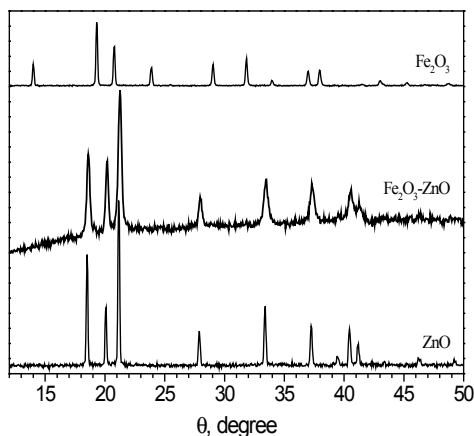


Figure 1. X-ray diffraction pattern of the initial ZnO and Fe_2O_3 and $\text{Fe}_2\text{O}_3\text{-ZnO}$ mechanochemically synthesized mixed oxide.

It had been found that all samples exhibit the hexagonal wurtzite structure in correspondance with the JCPDS database of card number 36–1451. Apart from a small decrease in peak intensity, the Fe-doping does not affect the ZnO wurtzite structure. The relative decrease in intensity of all XRD peaks in Fe-doped mixed oxide can be attributed to incorporation of Fe ions into the ZnO lattice and the resultant decrease of crystallite size.

This is also evidenced by the increase in the full width at half maxima (FWHM) of the XRD peaks in Fe-doping in the ZnO sample. This effect is due to the fact that Fe³⁺ ion has smaller radius (0.055 nm) than Zn²⁺ ion (0.074 nm) and doping results in contraction of the lattice parameters [6–8]. The spectra show only diffraction peaks of ZnO without any addition of other diffraction peaks. This might be due to a small quantity of iron, which can substitute the position of Zn ions in the ZnO structure. Therefore there is not change of peak positions, when doping ZnO with iron in this study.

Isopropanol is probe for selectivity in catalysts, because it can undergo both dehydrogenation to acetone and dehydration reaction to propene [14]. The results of catalytic test are summarized in Table 1. At it is seen in Table 1 the initial ZnO was not selective for propene formation. Fe₂O₃ is selective towards both acetone and propene formation. The selectivity to propene increased after introduction of small amount of iron into catalyst Fe₂O₃-ZnO (sample 2) in comparison to pure ZnO.

Table 1. *Catalytic performance in isopropanol conversion (wt.%)*

No	Sample	T, °C	propene	acetone	isopropanol
1	ZnO	280	–	60	40
		350	1	96	3
2	Fe ₂ O ₃ -ZnO	280	2	63	35
		350	8	82	10
3	Fe ₂ O ₃	280	5	12	83
		350	18	56	16

The potential catalytic activity of the samples was evaluated in gas phase by using isopropanol as a probe molecule. Gas chromatographic analysis of the reaction products indicates the production of expected organic products, acetone and propene, with all catalysts. The conversion of isopropanol proceeds through dehydration to propene and dehydrogenation to acetone with the selectivity depending on the type of materials. Pure zinc oxide exhibited dehydrogenation of isopropanol at 280–320°C. Its dehydrating efficiency to propene was less than dehydrogenating activity of initial ZnO and started only at 300°C. Acetone was the main product with the pure hematite. The selectivity to propene for hematite was 22% at 430°C at 100 5 isopropanol conversion.

The results from the photocatalytic activity testing using different kind of light for the illumination are represented in Table 2.

Table 2. Degrees of photocatalytic conversion of ethylene (10 000 ppm C_2H_4 , feed concentration) under illumination with different kinds of light, contact time $\tau_e = 4$ min, 30% RH and O_2 excess over Fe_2O_3 -ZnO and Degussa 25 TiO_2 for comparison

Photocatalyst coating 1mg cm^{-2}	Conversion of C_2H_4 , %	Type of illumination	Intensity of illumination $W\ cm^{-2}$	Distance of illumination cm
Fe_2O_3 -ZnO	4	UV-A	0.014	0
Fe_2O_3 -ZnO	9	UV-C	0.014	0
Fe_2O_3 -ZnO	12	Visible	8.9	50
Degussa 25 TiO_2	26.5	UV-A	0.014	0
Degussa 25 TiO_2	40	UV-C	0.014	0
Degussa 25 TiO_2	0	Visible	8.9	50

All the data in the table refer to maximal contact time of ethylene (4 min), optimal humidity (30% RH) and large excess of oxygen in the feed mixture. The degree of conversion of ethylene was taken as a measure of the photocatalytic activity of the sample. For the sake of comparison the performance of the Fe_2O_3 -ZnO photocatalytic material is juxtaposed with previous results, obtained with the standard reference photocatalyst Degussa P25 (75% anatase TiO_2 + 25% rutile TiO_2) [15]. It can be seen that Degussa P25 is superior in case of using UV light, while the composite Fe_2O_3 -ZnO material has also some activity with visible light, where Degussa displays zero activity.

The obtained results can be explained with the fact that the band gap of the Fe_2O_3 component is narrow (2.2 eV, corresponding to $\lambda=564$ nm i.e. activation by visible light), while the wide band gap of anatase TiO_2 (3.2 eV, corresponding to $\lambda=388$ nm) shows that it can be excited only by UV light. For this reason anatase TiO_2 displays zero activity with visible light, while the Fe_2O_3 -ZnO has some moderate activity with visible light. To the contrary – under UV light irradiation the TiO_2 has higher photonic efficiency than the Fe_2O_3 -ZnO composite material. At one and the same illumination intensity the UV-C lamps are more efficient than the black light blue lamps (UV-A light) probably because of the higher photon energy.

The mechanochemical technique can ensure obtaining the designed phases and structures by single step processing of materials in a closed activation chamber at room temperature. The multi-step character of mechanochemical activation involves the accumulation of energy due to

the formation of new surfaces, structural disorder in the bulk phase and even the change in the chemical composition of a solid.

CONCLUSIONS

Fe-doped ZnO mixed oxides were prepared by high energy ball milling and analyzed for structural, catalytic and photocatalytic properties. The XRD spectrum shows samples that exhibit wurtzite crystal structure which is not affected by Fe doping.

The reactivity of Fe₂O₃-ZnO mixed oxide as catalysts was investigated using the decomposition of isopropanol as model reaction. Pure ZnO is highly selective towards acetone formation. Dehydration and dehydrogenation of isopropanol are performed over Fe₂O₃-ZnO mixed oxide. The dehydrogenation of isopropanol to acetone was found to be dependent on the chemical composition of the samples.

The effect of the illumination on the photocatalytic activity of mechanochemically activated Fe₂O₃-ZnO mixed oxide (1% wt. Fe) was studied. The mechanochemically prepared Fe₂O₃-ZnO mixed oxide, shows absorption capacity in the visible region as well as in UV-region of solar spectrum that make this composite a promising heterojunction-type photocatalyst for solar light applications both for air purification from organics due to hole transfer from Fe₂O₃ valence band to ZnO valence band. The Fe₂O₃-ZnO mixed oxide is an effective photocatalyst for treatment of organic pollutant in air.

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