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Microemulsions in the preparation of highly active combustion catalysts

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Abstract

Catalytic activity in combustion of toluene in toluene–air mixtures and physical–chemical properties of platinum catalysts prepared from reverse microemulsions (water-in-oil) and by classical impregnation from water solutions of H_2PtCl_6 were studied. Microemulsion catalysts were more active than those prepared classically from water solutions. Size of Pt in classically impregnated catalysts was three times higher than that of catalysts prepared from microemulsions. In case of microemulsion preparation method, platinum is located near the pellet surface or its position in the pellet can be optimised. The effect of oil used in microemulsion system seems to be negligible for the activity of the catalysts with 0.1 wt.% Pt. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Life environment in the vicinity of chemical plants and solvent evaporation processes is often damaged by emissions of organic compounds (VOC) into the air. Catalytic combustion seems to be the most economic process how to decrease such emissions of volatile organic compound (VOC) [1–3]. In catalytic combustion process VOCs are oxidised at relatively low reaction temperature, which is determined by catalyst activity.

The activity of supported catalysts containing noble metals in combustion of VOC is affected by the type of catalyst support, type of noble metal, amount of active component in the catalyst, the way of catalyst preparation, etc. The distribution of the active component within the catalyst pellet and the diameter and shape of the active component particle [4] are closely connected with the method of preparation. With respect to the fact that the oxidation catalysts work at very high total conversion of organic compounds, higher than 95%, in a regime of external and internal diffusion, it is economically advantageous to locate the particles of noble metals on the outer part of the support particle. For that reason it is important to choose such a method of catalyst preparation which will ensure not only an optimal dispersion of active component in the catalyst but also its optimal location in the catalyst. There are various methods of catalyst preparation that can fulfill, to a different extent, the aim mentioned above. The most commonly practised techniques are incipient-wetness impregnation with a metal salt solution, ion exchange with a metal-containing cation or anion or the use of organometallic complexes as precursors [5]. The use of microemulsion (a reverse micellar system) could be another preparation method promising formation of

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very small metal particles, uniform in size, located on the external surface of the support. The method may be defined as a formation of optically transparent, thermodynamically stable dispersion of two immiscible liquids (water solution of metal salt and organic oil) consisting of nano-size domains of one or both liquids in the other, stabilised by an interfacial film of surface active molecules [6]. With the method of microemulsion, particles of a defined shape and diameter can be prepared. In general, very narrow distribution of particle size in the region of nanometer units can be obtained. A proper choice of a support (characterised by its surface area, by porous structure and chemical composition) can contribute to a stabilisation of the size and form of the originated nanoparticles and thus the improvement of the preparation method. After Pillai et al. [6], the dimensions of nanoparticles obtained from microemulsion are determined by the properties of the organic solvent used, the type of surfactant and hydrodynamic conditions applied during the preparation of the emulsion. The method of microemulsion was used by Boutonnet et al. [7] in the preparation of hydrogenation catalysts. They described a synthesis of platinum, palladium or rhodium nanoparticles of diameter in the range of 3–5 nm by reduction of a corresponding metal salt dissolved in a water–oil microemulsion.

Up to now, the microemulsion method of preparation was not used for preparation of oxidation catalysts applied in the process of catalytic combustion. The aim of our study was to prepare platinum oxidation catalyst by the microemulsion method, evaluate the physical and catalytic properties and compare them with the properties of catalysts prepared by conventional preparation methods.

2. Experimental

2.1. Catalyst preparation

Two types of support, γ-alumina in the form of full pellets (calcined at 500 °C) and θ-alumina in the form of hollow pellets (calcined at 900 °C), both manufactured in Chemopetrol Litvínov, Czech Republic, were used. The properties of the supports are given in Table 1.

Table 1
Physical properties of the supports

	Catalyst support	
	33-00	40-31
Dimension of pellet (mm)	5 × 5	4.5 × 4.5, hole 1.8
Bed density (g/cm^3)	726	662
RTG analysis	γ-Al_2O_3	θ-Al_2O_3
Surface area (m^2/g)	166	145
Pore volume (cm^3/g)	0.459	0.445
Porosity (%)	54	54
Pore radius (4V/S, nm)	7.0	8.1
Mesoporous radius (nm)	3.6, 4.4, 20	6, 35
Particle density (cm^3/g)	1.167	1.223
Skeletal density (g/cm^3)	2.509	2.683
Water absorption capacity (%)	40	50

The catalysts with 0.3, 0.2, 0.1 and 0.05 wt.% Pt were prepared by impregnation with H_2PtCl_6–water solutions or Pt microemulsions. Microemulsions were prepared from oil (cyclohexanol, cyclohexane or heptane), Tween 80 (surfactant) and water. The value R (mol H_2O/mol surfactant) moved in the range 300–1100. Chloroplatinic acid was added to microemulsions prepared in such amounts that the catalysts with demanded amounts of Pt were obtained. The catalysts were dried 4 h at 120–160 °C and calcined at 500 °C (if not mentioned otherwise).

2.2. Characterisation of the catalysts

Surface area. Surface areas of the supports were determined from desorption isotherms of nitrogen adsorbed at −198 °C after evacuation at 350 °C for 5 h on ASAP 2010, Micromeritics, USA.

Pore size distribution. Pore size distributions were obtained from mercury porosimetry working in the range 0.1–400 MPa (AutoPore III, Micromeritics, USA).

Size of platinum particles. Transmission electron microscopy (TEM) was performed to determine the size of the Pt particles supported on alumina and check the dispersion of the platinum particles. TEM studies were performed on a TOPCON EM002B apparatus with a top entry device and operating at 200 kV (resolution 0.18 nm).

Distribution of Pt throughout the catalyst pellet. Electron microprobe Jeol JXA-50A equipped with an energy dispersive X-ray spectrometer EDAX TV 9400 was used for the determination of platinum concentration as a function of the position in a pellet.

Catalytic experiment. Catalytic experiments were done with 75 ml of a catalyst and $F/W = 10\,000\,\mathrm{m^3}/(\mathrm{h\,kg_{cat}})$. Combustion of toluene was chosen as a model VOC and non-steady-state reaction condition (linear increase 3.5 °C/min in reaction temperature) was applied in the catalyst activity evaluation. The concentration of toluene in air was $1\,\mathrm{g/m^3}$. Temperatures of gaseous reaction mixture entering and leaving the catalyst layer were measured by thermocouples. Inlet temperatures T_{50} or T_{90}, at which 50 or 90% conversions of toluene were achieved, were taken as a measure of catalytic activity.

3. Results and discussion

3.1. Catalytic activity

Catalysts with 0.1 wt.% of Pt were prepared over two supports (γ- and θ-alumina) using both microemulsions and water solutions of chloroplatinic

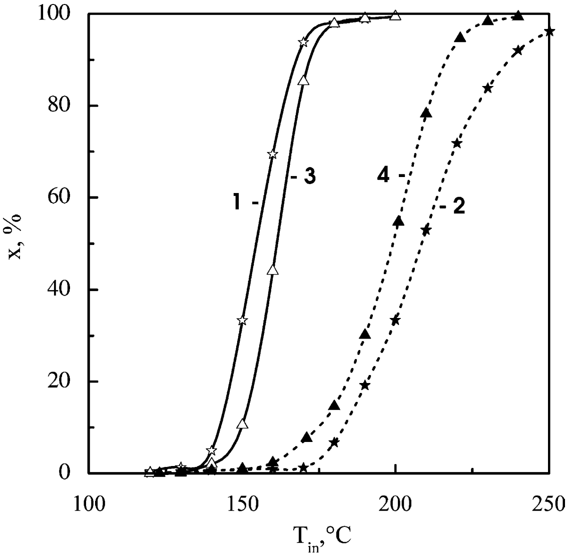

Fig. 1. Light-off curves of toluene obtained with platinum catalysts prepared by impregnation of γ-alumina (curves 1, 2) and θ-alumina (curves 3, 4) by heptane–Tween 80–water microemulsion (curves 1, 3) or water solution of H_2PtCl_6 (curves 2, 4).

Table 2
Survey of the catalysts prepared over γ-alumina and θ-alumina supports

Sample[a]	Support	Pt (wt.%)	Microemulsion			Catalytic activity (°C)	
			Oil	R	Pt[b] (mmol/l)	T_{50}	T_{90}
M02	33-00	0.3	Cyclohexanol	1004	124.2	152	171
M03	33-00	0.1	Cyclohexanol	1004	44.3	157	173
M04	33-00	0.05	Cyclohexanol	1004	22.5	168	183
M05	33-00	0.3	Cyclohexane	1004	128.5	143	158
M06	33-00	0.1	Cyclohexane	1004	45.9	153	174
M12	33-00	0.1	Cyclohexane	352	20.5	157	172
M07	33-00	0.1	Cyclohexane/cyclohexanol	1004	45.1	153	170
M10	33-00	0.1	Heptane	889	67.7	155	169
M13	33-00	0.1	Heptane	1067	45.9	155	168
M09	33-00	0.1	Heptane	1067	45.6	150	168
M11	33-00	0.1	Heptane	1036	33.9	155	170
M15	33-00	0.1	Heptane	336	30.8	159	171
M16	33-00	0.1	Heptane	340	23.6	155	170
B01[c]	33-00	0.2	Hexadecane	×	×	168	182
I01	33-00	0.1	Water	–	28.9	204	224
I02	33-00	0.3	Water	–	9.8	209	237
M19	40-31	0.3	Heptane	1004	104.9	140	153
M24	40-31	0.3	Cyclohexanol	527	212	143	154
M25	40-31	0.3	Heptane	1004	47.4	144	154
M20	40-31	0.1	Heptane	1004	37.0	161	172
B02	40-31	0.2	Hexadecane	×	×	153	166
I03	40-31	0.3	Water	–	27.4	183	200

[a] M denotes microemulsion, I denotes impregnation from water solution of H_2PtCl_6.
[b] Concentration of Pt in water.
[c] Prepared by M. Boutonnet, KTH Stockholm.

acid. The activity of the catalysts in combustion of toluene is depicted in Fig. 1. Evidently, both catalysts prepared from microemulsions are more active (the temperature T_{50} is about 50 °C lower) than the catalysts prepared by classical impregnation methods. To study the problem of microemulsion impregnation more completely, some other catalysts differing in Pt concentration (0.3, 0.2, 0.1 and 0.05 wt.% Pt), type of oil and molar ratio R of water to surfactant were prepared. Their catalytic activities are summarised in Table 2.

It is not surprising that higher concentration of platinum in the microemulsion catalysts in the concentration range 0.05–0.3 wt.% Pt lead to lower T_{50} temperature, i.e. to higher catalytic activity.

The effect of the support on the microemulsion catalyst activity is not obvious. Though the alumina-based supports differ in their physical properties (Table 1), especially in radius of mesopores, water absorption capacity and sorption ability, the combustion activities of Pt catalysts are very similar. Evidently, some other parameters are important for obtaining the highest catalytic combustion activity.

Detailed examination of the catalytic data shows that there is not a great difference in the combustion activity when different oils are used in microemulsion preparation. For the catalysts having 0.1 wt.% of platinum the T_{50} temperature moves within the range 150–161 °C. The effect of R (water/surfactant molar ratio; in the range 336–1067) on the catalyst activity was also not very distinct.

The results given in Table 2 confirm that all catalysts prepared from microemulsions are much more active than the catalysts prepared by classical impregnation from water solutions. The reason of such findings could be a different distribution of platinum concentration in the pellets.

3.2. Concentration profiles of Pt in a catalyst pellet

An example of platinum concentration throughout the catalyst pellets prepared by impregnation of θ-alumina hollow pellets (pellet radius 2.25 mm) by microemulsions and water solutions of chloroplatinic acid are shown in Fig. 2. The M19 and M24 catalysts

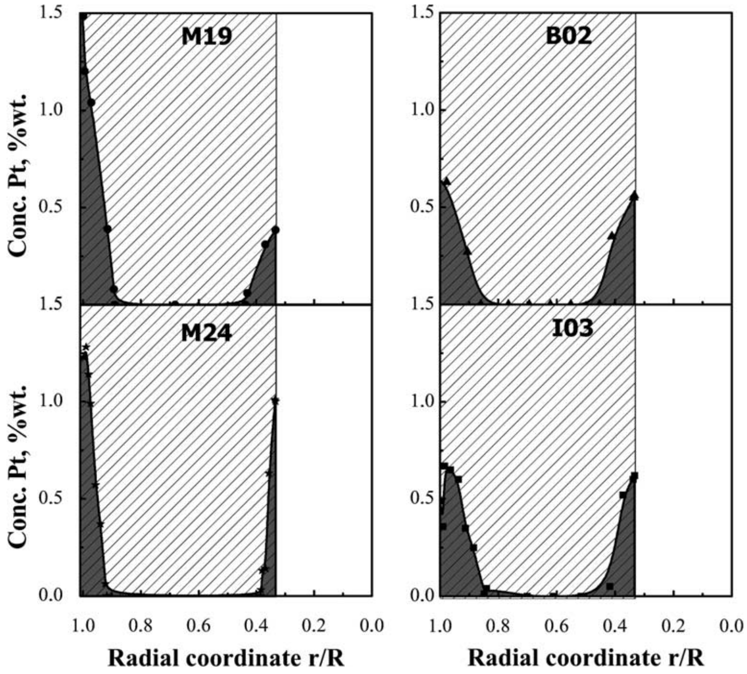

Fig. 2. Concentration of platinum within the microemulsion catalysts (M19, M24, B02) and impregnated catalyst (I03) prepared over θ-alumina (pellet radius 2.25 mm).

show very high concentration on the outer part of the pellets (1.25–1.50 wt.%), while the I03 catalyst, classically impregnated, only 0.6 wt.%. As combustion of organic compounds proceeds in the regime of outer and internal diffusion, i.e. at high reaction rate of surface reaction, the overall reaction rate is determined by the rate of transport of the reactant to the catalyst surface. Higher concentrations of platinum on the pellet surface accessible to the reactants lead to higher conversions of reactant. It is important to note that the properties of the microemulsion can affect the concentration of platinum inside the pellet hole (compare the profiles of M19 and M24 catalysts). A microemulsion of high viscosity (which is the case of microemulsion used in the preparation of M19) cannot enter the hole of the pellets easily and in such an instance, the Pt concentration in this part of the pellet is lower.

The platinum concentration profile of the B02 catalyst (prepared also from microemulsion) is similar to that of the impregnated I03 catalyst. However, its catalytic activity is higher (the T_{50} temperature is lower by 30 °C compared to the temperature of corresponding impregnated I03 catalysts). Evidently, the concentration of Pt in the outer shell of the catalyst is not the only parameter responsible for the catalytic activity.

3.3. Platinum particle size

TEM measurements revealed (Fig. 3) that the typical size of platinum in the calcined catalyst differs very much depending on the way the catalyst was prepared.

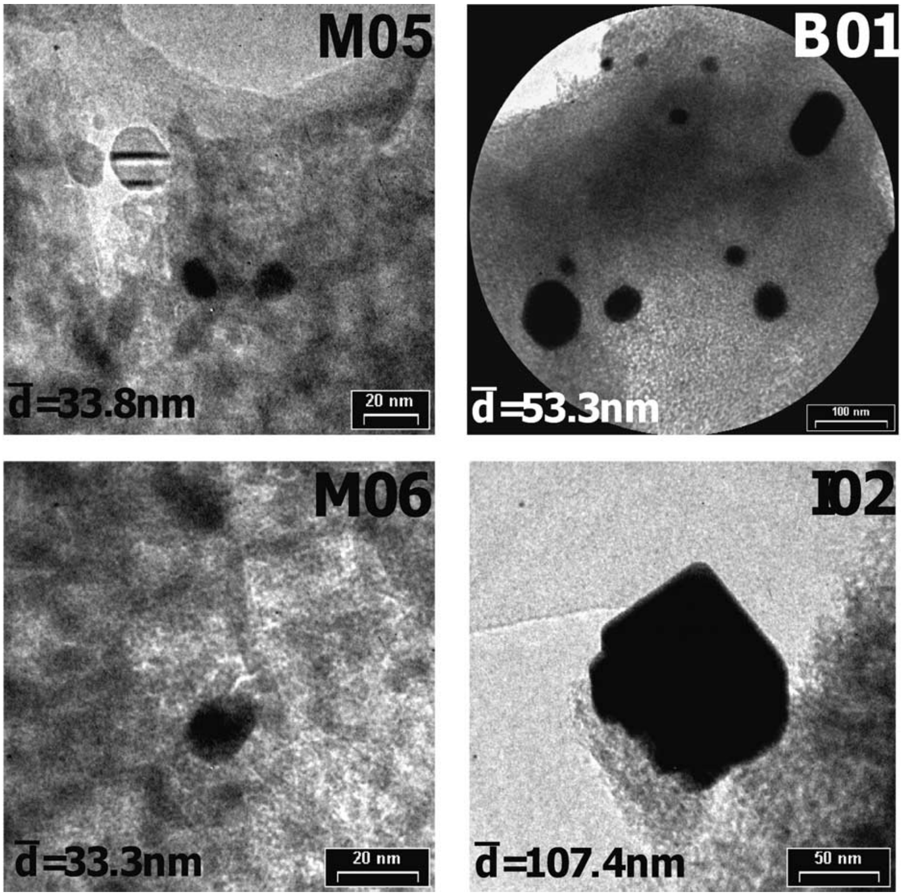

Fig. 3. TEM micrographs of platinum particles determined in microemulsion catalysts (M05, M06, B01) and in the I02 catalyst prepared classically by impregnation with water solution of H_2PtCl_6 (*d* represents the mean arithmetic diameter of the Pt particles).

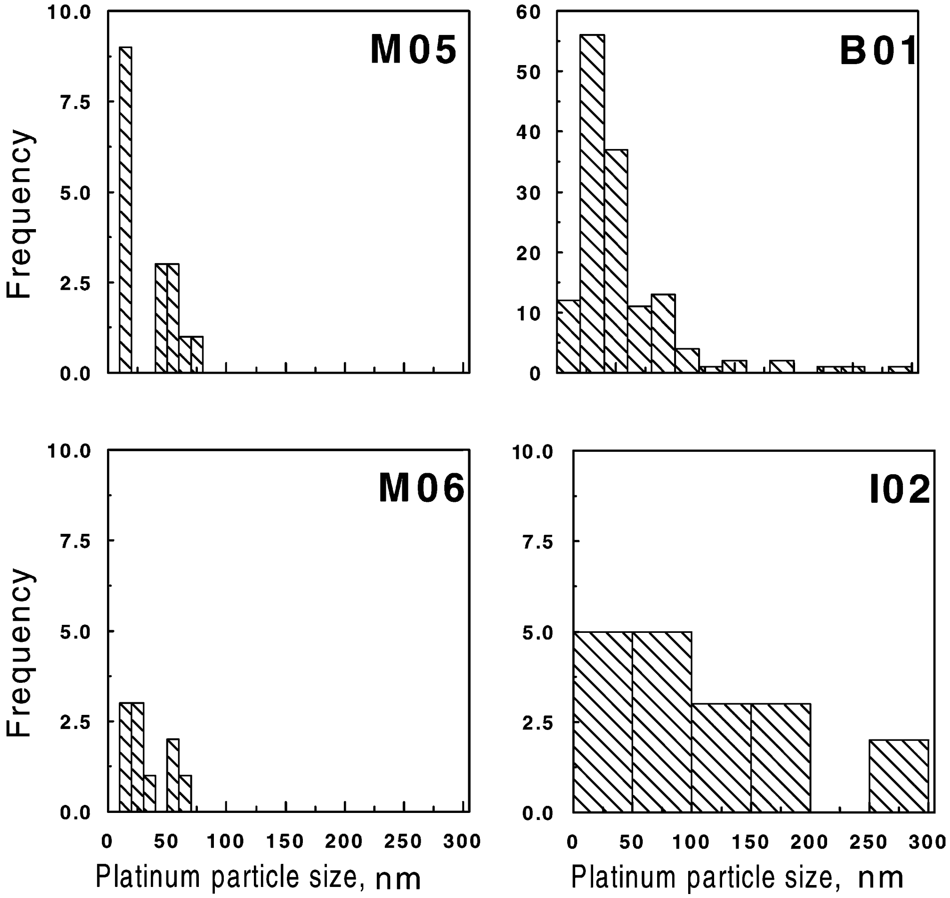

Fig. 4. Histograms of platinum particle sizes determined by TEM in microemulsion catalysts (M05, M06, B01) and in the I02 catalyst prepared classically by impregnation with water solution of H_2PtCl_6.

The microemulsion catalysts exhibit similar and relatively small platinum particles with diameter around 35 nm. On the other hand, the impregnated I02 catalyst has larger particles. The examination of greater numbers of platinum particles in the studied catalysts gave the following findings (Fig. 4): the microemulsion catalysts have narrower particle size distribution located between 5 and 90 nm, while the impregnated I02 catalyst has a much broader distribution reaching diameters up to around 300 nm.

The platinum particle sizes found in our calcined oxidation catalysts are much larger than those observed [8] in the reduced microemulsion catalysts moving in the range 0.5–3.5 nm. Calcination in air of platinum catalysts including microemulsion catalysts apparently evolves a growth of primary platinum particles by a sintering process.

3.4. Effect of calcination conditions

As calcination of the catalysts leads to different platinum particle sizes, we examined the effect of calcination conditions of microemulsion catalysts on the catalytic activities in combustion of toluene. We compared (Table 3) the activity of the catalyst calcined under static conditions, in the flow of air and non-calcined catalysts. By repeating the catalytic tests we tried to estimate the stability of the catalyst activity. We found that the best initial combustion activity was showed by the M13 catalyst which was calcined

Table 3
Effect of calcination conditions on the catalytic activity (all catalysts with 0.1 wt.% Pt were prepared from heptane–Tween 80–water microemulsions with $R = 1004$)

Sample	Oil	T_{50} (°C)			Calcination conditions
		Test 1	Test 2	Test 3	
M13	Heptane	151	155	–	500 °C, air flow 6000 l/(l_{cat} h)
M14	Heptane	158	157	–	500 °C, static conditions
M06	Cyclohexane	153	153	–	500 °C, air flow 6000 l/(l_{cat} h)
M08	Cyclohexane	205	160	160	Dried at 200 °C

in air flow at 500 °C. The temperature T_{50} of repeated test decreased only a little (by 4 °C). After calcination of the sample under static conditions the catalyst activity was somewhat lower, but the activity did not change in repeated tests. The M06 catalyst prepared from a cyclohexane–Tween 80–water microemulsion and calcined in the flow of air at 500 °C showed high and stable catalytic activity. However, when this catalyst was tested in a dried state (200 °C) the initial catalytic activity was very low ($T_{50} = 205$ °C) but improved during repeated catalytic tests to $T_{50} = 160$ °C.

4. Conclusion

Experimental data showed that the catalysts prepared on both γ- and θ-alumina from microemulsions were more active than the catalysts prepared by classical impregnation of the supports with water solutions of chloroplatinic acid. The T_{50} temperatures of toluene combustion moved in the range 200–210 °C for the impregnated catalysts (0.1 wt.% Pt), whereas temperatures 150–160 °C were sufficient for similar catalysts prepared from microemulsions. TEM proved smaller platinum particles sizes (10–60 nm) in the microemulsion catalysts in contrast to larger size and broader particle size distribution of platinum (50–300 nm) in classically impregnated catalysts. High activity of the catalysts from microemulsions can also be accounted for by a higher concentration of platinum in the outer shell of catalyst pellets (found by electron microprobe). The effect of organic phase (oil) used in microemulsion system seems to be negligible for achieving high activity of the platinum catalysts.

Properties of microemulsions apparently play an important role in the preparation of platinum oxidation catalysts. Small amount of water in reverse microemulsions does not allow platinum compound to enter deeply into the catalyst pellet. Moreover, proper preparation of a reverse microemulsion can lead to formation of small droplets, uniform in size, which can result in optimised platinum particle size of oxidation catalysts.

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