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INFLUENCE OF SILVER DISPERSITY ON ITS SPECIFIC CATALYTIC ACTIVITY IN ETHYLENE OXIDATION

S.N. Filimonova, S.N. Goncharova and A.V. Khasin

Institute of Catalysis, Novosibirsk 630090, USSR

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Specific catalytic activity for massive (powders and films) and supported (Ag/SiO_2) silver catalysts have been studied in ethylene oxidation. It has been found to be approximately constant for metal particles whose size is above 30 nm.

Исследована удельная каталитическая активность серебряных катализаторов, массивных (порошков, пленок) и нанесенных (Ag/SiO_2), в отношении реакции окисления этилена. Найдено приблизительное постоянство удельной каталитической активности серебра в исследованной области размеров частиц металла выше 30 нм.

As long as 25 years ago Belaya and Rubanic came to the conclusion that irrespective of the preparation method, pure silver had approximately the same specific activity in ethylene oxidation [1]. They examined various samples of silver catalysts with $S \leqslant 1\ m^2/g$. Later on several investigations of the catalytic oxidation of ethylene were carried out over high-dispersity supported silver catalysts [2-8]. Studies of the last 15 years raised the question about the influence of the size of silver particles on its specific catalytic activity. So far this question has not been answered due to the fact that the data obtained are conflicting. There is considerable discrepancy of the literature data concerning the character of

Akadémiai Kiadó, Budapest

this dependence and the specific activity values [4-8]. It must be noted that the dependence of specific catalytic activity on the size of metal particles is observed in the range of 30-100 [4,7,8], i.e. far beyond the region of microcrystalline state of the metal (≤ 5 nm). For this region noticeable changes in the electron and structural properties of metallic phases are most probable.

It is possible that the reason for the discrepancy in the literature data is the different concentration of admixtures in supported silver. In several studies to obtain silver particles of different sizes, samples of supported catalysts were subjected to high-temperature sintering. In this case considerable diffusion of admixtures from the carrier into bulk and towards the silver particle surface is possible [4,7]. The other reason for the observed discrepancies can be the competitive formation of carbon on the metal surface, whose accumulation depends on the reaction conditions and time.

To elucidate the effect of silver dispersity on its specific catalytic activity, we have compared the specific activity of supported silver (Ag/SiO_2) having particles whose size is ranging in that region, with that of silver powders and films consisting of much larger metal particles. We have applied methods that prevent accumulation of admixtures in metal during catalyst preparation and determination of catalytic activity.

EXPERIMENTAL AND DISCUSSION

Supported catalysts were prepared by impregnating the carrier with an aqueous solution of silver nitrate, subsequent drying and reduction by hydrogen. SKh-1.5 silica gel ($S=41\ m^2/g$ with an overall pore volume of $1.5\ cm^3/g$) which is inert towards isomerization of ethylene oxide, was used as a carrier. The overall concentration of admixtures in the carrier was not more than 0.15 wt.%. Immediately before impregnation, the carrier was heated in flowing helium at 573 K for

4 h. To obtain samples having different average sizes of metal particles, the silver content in the catalysts was varied by varying the concentration of the impregnating solution. Drying after impregnation was carried out with an IR lamp at T ~ 330 K in air. Catalysts were reduced at 473 K by a diluted hydrogen mixture (1% H_2 + 99% He) and then by pure hydrogen. Average size of silver crystallites in the catalysts obtained was determined from oxygen chemisorption data and also by electron microscopic and X-ray diffraction methods. The structural characteristics are listed in Table 1.

Powdered silver was prepared by hydrogen reduction at 473K of washed and dried silver oxide precipitated from a solution of silver nitrate by potassium hydroxide. S_{BET} of the sample determined according to low-temperature adsorption of krypton was 0.4 m^2/g. This value corresponds to an average silver particle size of about 1400 nm, which agrees with data from scanning electron microscopy.

Silver films were prepared in vacuum ($\sim 10^{-4}$ Pa) by metal vaporization from a molybdenum wire heated by electric current, and condensation of its vapors on the walls of the quartz reaction vessel cooled by water. Freshly condensed films were sintered in vacuum at 473 K for 2 h. The surface area of condensed silver was determined by multiplying the geometrical surface area of the films by the roughness factor taken to be equal to 1.5.

Catalytic activity was determined by a flow-circulation method at 448 K and approximately atmospheric pressure of the gas mixture of reactants with helium containing 1 vol.% ethylene and 7 vol.% O_2. Each time catalytic reactions and determinations of the catalytic activity of supported catalysts and powdered silver were preceded by sample pretreatment by oxygen and hydrogen at 473 K. Due to this pretreatment, the same initial state of catalysts was attained, which is considered as a standard state. Catalytic activity of films was determined immediately after their preparation without previous gas treat-

Table 1

Specific catalytic activity of silver catalysts (T=448 K, $P_{C_2H_4}=1\times10^3$ Pa, $P_{O_2}=8\times10^3$ Pa)

Catalyst	Ag content (wt.%)	Specific surface area of silver (m^2/g Ag)	Average size of particles (nm)				Catalytic activity of Ag $\left(\frac{\text{molec.}C_2H_4}{m^2\cdot s}\right)$		Selectivity (%)
			Adsorption data	X-ray data	Electron microscopy data				
					$d=\frac{\Sigma n_i d_i}{\Sigma n_i}$	$d'=\frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2}$	$W_1\times10^{-17}$	$W_2\times10^{-17}$	
Ag/SiO_2	1.87	6.7	86	60	26	63	2.5	0.82	25
Ag/SiO_2	0.55	21.0	27	17	15	24	2.5	0.98	28
Ag/SiO_2	0.55	16.6	34	32			1.7	0.65	28
Ag/SiO_2	0.24	20.7	28		7	16	1.2	0.36	23
Ag (powder)	100	0.4	1400				3.5	1.5	30
Ag (film)	100						3.7	1.6	30

ment. The degree of ethylene conversion did not exceed 20 %. At the above low reaction temperature and conversion degrees of ethylene, further oxidation of the product ethylene oxide can be neglected. Under the conditions examined with increasing time, the catalytic activity of supported catalysts and powdered silver varies only slightly, whereas that of films significantly decreases. For 10 h reaction their activity decreased by 2-3 times compared to the value found after 1 h reaction.

Structural characteristics for the catalysts examined and reaction rate determined after 1 h reaction for the deep oxidation of ethylene (W_1) and ethylene oxidation to ethylene oxide (W_2) as well as formation selectivities for the latter are listed in Table 1. Specific catalytic activities of silver in supported catalysts with ~ 30 and 90 nm particles differ on the average by not more 1.5 times and are 2-3 times lower than the specific activity of powders and films.

Thus the results suggest that the initial specific catalytic activity of silver that is characteristic for the standard properties of silver containing no carbon formed is approximately the same in the examined range of particle sizes above 30 nm.

It is possible, however, that the dispersity and surface structure of silver are of significant importance for the intensity of carbon formation accompanying catalytic oxidation and deactivating catalyst. It is this reason as well as the effect of admixture, that can be responsible for the reported low specific activities for $\geqslant$ 30 nm silver particles considerably deviating from their standard values.

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