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Different morphologies of silver nanoparticles as catalysts for the selective oxidation of styrene in the gas phase

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Silver nanoparticles of different morphologies were prepared using the polyol process and then dispersed on α-alumina. Catalysts were tested for the selective oxidation of styrene in the gas phase. Activity and selectivity were strongly dependent on the morphology of the silver nanoparticles.

Silver catalysts have become increasingly important in the selective oxidation of olefins for the synthesis of industrially interesting products such as epoxides and aldehydes.[1] Metal nanoparticles have attracted considerable attention because of their novel physical properties and their potential applications in areas such as catalysis.[2] Recently, silver nanoparticles have been synthesised by reducing silver nitrate with ethylene glycol in the presence of poly(vinylpyrrolidone) (PVP) *via* a polyol process.[3–5] It is well known that the activity and selectivity of catalyst nanoparticles are strongly dependent on their size, shape and surface structure, as well as on their bulk and surface composition.[6] The shape-controlled synthesis of metal nanoparticles can open up a new world of heterogeneous catalysis. This approach may help to understand the effect of crystal planes on chemical reactivity.[7] Oriented nanoparticles could also be extended to industrial applications to obtain many useful chemicals. In these regards, catalysts obtained from silver nanoparticles seem to be particularly interesting for studying the selective oxidation of olefins with oxygen as oxidant because it has been demonstrated that silver is a selective catalyst for olefin epoxidation.[8]

This study investigates how different morphologies of silver nanoparticles supported on α-Al_2O_3 and MgO affect the selective oxidation of styrene in the gas phase using oxygen as oxidant. The promotion effect of potassium hydroxide on the catalytic activity has also been investigated.

The catalysts were prepared by two procedures. In the first, the wetness impregnation method was used to impregnate α-Al_2O_3 and MgO supports with an appropriate amount of an aqueous solution of silver nitrate to obtain 15 and 40 wt% of silver, respectively. In the second, silver nanoparticles (11 wt%) were dispersed on α-Al_2O_3 with an acetone solution. The silver nanoparticles were synthesized *via* a polyol process. In a typical synthesis of silver nanoparticles, 30 ml ethylene glycol solution of $AgNO_3$ (0.25 M, Aldrich) and 30 ml ethylene glycol solution of PVP (0.375 M in repeating unit weight-average molecular weight ≈ 40 000, Aldrich) were simultaneously added in 50 ml ethylene glycol at 433 K under vigorous stirring. The reaction mixture was then refluxed for 45 minutes at this temperature. The nanoparticles obtained were diluted with acetone (about 10 times by volume) and separated from ethylene glycol by centrifugation at 4000 rpm for 20 minutes. Silver nanoparticles were also prepared with a PVP/$AgNO_3$ molar ratio of 3. The catalysts were dried in an oven at 393 K for 24 hours and reduced in H_2 at 623 K for 3 hours before the characterization and the activity tests.

The samples were structurally characterized using X-ray diffraction (XRD), temperature programmed reduction (TPR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV–vis absorption spectroscopy. The selective oxidation of styrene in gas phase at 573 K was carried out in a continuous fixed-bed reactor over 1.0 g catalyst at atmospheric pressure. The catalytic tests were operated at different styrene : O_2 : Ar molar ratios. The feed gas mixture (O_2, Ar) was delivered by means of mass flow controllers and the styrene was introduced into the reactor by a pump. The products were analysed by a Shimadzu GC 2010 gas chromatograph equipped with a capillary column and FID detector.

Fig. 1 shows the morphologies of the catalysts observed by SEM with a JEOL JSM-35C scanning microscope operated at an acceleration voltage of 15 kV.

The morphologies of the silver nanoparticles prepared by the polyol process were found to depend heavily on the experimental conditions such as temperature and the molar ratio between PVP and $AgNO_3$. Previous studies have suggested that the degree of polymerization of PVP (the average number of repeating units in one PVP molecule) also plays an important role in determining the morphology of the silver nanoparticles.[9] We obtained silver nanowires (Fig. 1a) when the molar ratio of PVP and $AgNO_3$ was 1.5. These nanowires had a mean diameter of 150 nm. This was consistent with TEM results. When the molar ratio was increased from 1.5 to 3, nanopolyhedra were the major product (Fig. 1b). The SEM image of the 40% Ag/MgO catalyst (Fig. 1c) prepared by impregnation shows the presence of silver nanowires and other silver particles dominated by irregular shapes with diameters between 100 nm and 500 nm. Irregularly shaped particles with diameters between 200 nm and 1000 nm (Fig. 1d) were also observed for the 15% Ag/α-Al_2O_3 catalyst prepared by wetness impregnation using a silver nitrate solution.

The X-ray diffraction of the nanowires and nanopolyhedra synthesized using the polyol process suggested that silver existed purely in a face-centered cubic structure (Fig. 2). The X-ray powder diffraction (XRD) patterns were recorded using a Siemens D5000 diffractometer using nickel filtered Cu Kα radiation (λ = 1.54056 Å) in 2θ ranging from 30° to 80°.

The diffraction did not suggest the presence of possible impurities such as Ag_2O and $AgNO_3$. The three peaks detected for the silver nanoparticles were assigned to diffraction from the (111), (200) and (220) planes of fcc silver, respectively. The lattice constants calculated by XRD for the nanowires and nanopolyhedra were 4.0839 and 4.0872 Å, respectively, which are very close to the report data (a = 4.0862 Å, Joint Committee on Powder Diffraction Standards file 04–0783). The ratio of intensity between the (111)

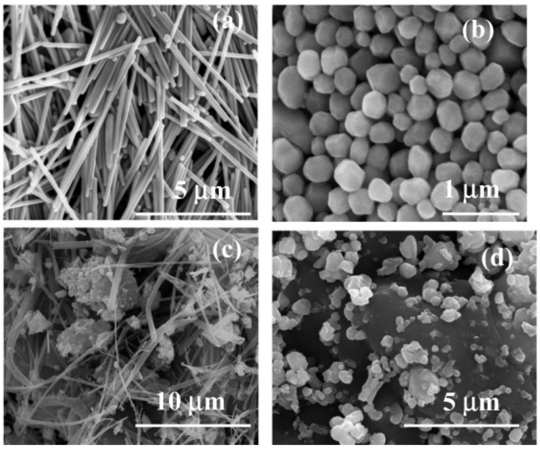

Fig. 1 SEM images of silver catalysts.

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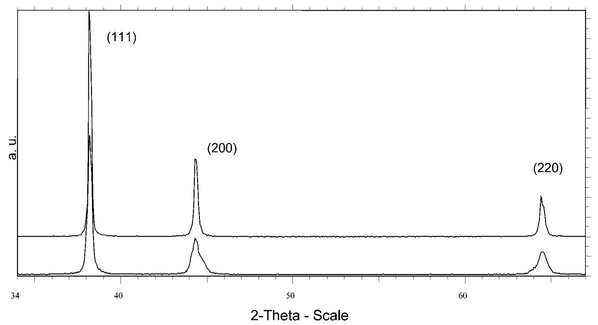

Fig. 2 XRD pattern of silver nanowires (lower pattern) and nanopolyhedra (upper pattern).

and (200) peaks has values of 4.5 and 2.5 for nanowires and nanopolyhedra, respectively. For the nanowires, this ratio is higher than the standard file (JCPDS) (4.5 *versus* 2.5) indicating that the nanowires were abundant in (111) facets probably because of their external morphology. Nanowires and nanopolyhedra tend to grow as bicrystals twinned along the (111) planes, showing (111) crystal faces at their surface.[10] The UV–Vis spectrum of the nanowire solution showed a broad peak at *ca.* 380 nm, which may arise from the surface plasmon excitation of the silver nanostructures, as has been previously reported.[11]

Fig. 3a, b shows the TPR profiles of the 11% silver nanowire supported on α-Al_2O_3 and 15% Ag/α-Al_2O_3 catalysts after treatment in O_2 for 1 hour at 623 K. The figure shows two broad peaks for the nanowire catalyst at around 633 K (most intense peak) and 873 K. The 40% Ag/MgO and nanopolyhedron catalysts show similar behaviour. These peaks have been attributed to different oxygen species (O_β, O_γ).[12] However, for the 15% Ag/α-Al_2O_3 catalyst they are shifted to higher temperatures (753 and 933 K, respectively). The most intense peak for this catalyst is the second one but they are both lower than the peaks obtained from nanowires.

The results indicated that the oxidation treatment before the TPR analysis oxidizes a small amount of Ag to Ag_2O. By measuring the H_2 consumption we found that the silver oxidation content of the catalysts was 0.35%, 0.8%, 1.1% and 1.5%, for 15% Ag/α-Al_2O_3, 40% Ag/MgO, nanopolyhedron and nanowire catalysts, respectively. The selective oxidation of styrene (Table 1), at steady state, over Ag catalysts shows phenylacetaldehyde (Phe) and styrene oxide (SO) as the main products. The direct combustion route of styrene was negligible for silver nanowires and nanopolyhedra even at near total conversion. However, the 15% Ag/α-Al_2O_3 catalyst shows around 30% of total combustion products even at lower conversion (around 5%). The addition of KOH on the nanowires improves the catalytic activity. The increase in the O_2 : styrene molar ratio also improves the conversion while the selectivity to SO decreases. Substantial quantities of phenylacetaldehyde were produced when styrene oxide was heated at the reaction temperature studied. It is highly possible that the phenylacetaldehyde obtained in the reaction is formed from the thermolysis of the styrene oxide.[13] A comparison of the reaction activity and selectivity with the results of the TPR profiles suggests that the first peak is responsible for the different performance and that it is related to oxygen species that preferentially lead to high activity and selectivity.

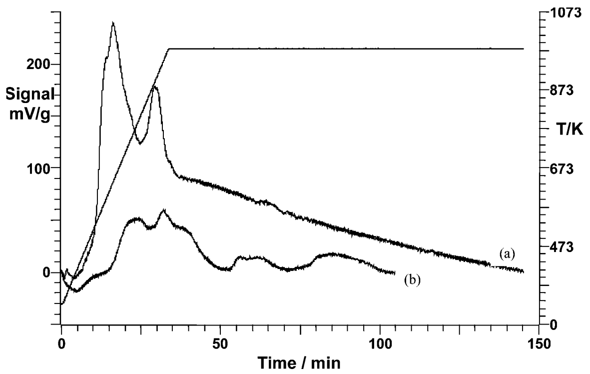

Fig. 3 TPR profiles obtained from fresh catalysts (a) 11% silver nanowires supported on α-Al_2O_3, (b) 15% Ag/α-Al_2O_3.

Table 1 Results for the selective oxidation of styrene[b]

Catalyst[a]	Conversion of styrene (%)	Selectivity (%) Phe	SO
15% Ag/α-Al_2O_3	4.9	53.2	15.6
11% $Ag^{(NW)}$/α-Al_2O_3	57.6	57.5	42.5
11% $Ag^{(NW)}$/αAl_2O_3[c]	66.7	79.5	20.5
11% $Ag^{(NW)}$/αAl_2O_3[c,d]	93.2	82.7	17.3
11% $Ag^{(NW)}$/αAl_2O_3[c,e]	96.4	94.5	5.5
11% $Ag^{(NP)}$/αAl_2O_3	57.5	69.2	30.8
40% $Ag^{(NW)}$/MgO	77.1	82.9	17.1

[a] (NW) nanowires; (NP) nanopolyhedra. [b] Feed: 50 O_2 : 1 styrene (mol%), reaction temperature at 573 K. [c] 400 ppm KOH referred to Ag. [d] 65 O_2 : 1 styrene (mol%). [e] 100 O_2 : 1 styrene (mol%).

In summary, we report the synthesis of Ag nanoparticles using poly(vinylpyrrolidone) (PVP) as the template. Two nanoparticles were obtained: silver nanowires and nanopolyhedra. The top crystal face of these nanoparticles was (111), which may have a beneficial effect on the selective oxidation of styrene. The morphology and the chemical composition of the silver catalyst determined the activity and selectivity for the styrene oxidation reaction. These differences can be explained if it is taken into account that TPR confirmed the presence of different oxygen species in the silver catalyst. It was found that the catalytic performance of the Ag nanowires for the selective oxidation of styrene can be improved by increasing the basic character of the catalyst, as well as the O_2 : styrene molar ratio. The synthesis of silver nanoparticles with a shape controller has potential applications for the selective oxidation of olefins.

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