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Preparation of structured egg-shell catalysts for selective oxidations by the ANOF technique

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Abstract

Shell-type catalysts supported on metal wires were prepared by anodic oxidation with spark discharge (the “ANOF” technique) in the presence of precursors of the catalytically active phase. Aluminium, magnesium and titanium oxide were employed as carriers, whereas nickel (also doped with lithium), chromium or molybdenum were the active components. The carrier oxides displayed regular pore structures determined by the preparation condition and influenced by the precursor of the active component, which was incorporated in the pore system of the carrier during the anodisation process. The nickel-containing catalysts were found to yield 60–90% cyclohexene selectivity in the oxidation of cyclohexane. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Egg-shell catalysts; ANOF technique; Shell-type catalysts

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1. Introduction

In many catalytic reactions occurring on solid catalysts, the irregular pore system of the catalyst may negatively influence the selectivity of a desired intermediate product by slowing down the diffusion of the product molecules in the tortuous pores, thus allowing their further conversion to undesired by-products. We have developed therefore, by using the anodic oxidation technique, a new type of shell catalysts consisting of alumina supported on aluminium wires, which possess very regular and short pores [1,2]. It was shown that such catalysts allowed the control of selectivity in heterogeneously catalysed oxidation of hydrocarbons [3–5] or in hydrogenation reactions [6]. The structure of the porous anodic alumina films was characterised as a close-packed array of hexagonal cells, each of them containing a central cylindrical pore directed towards the bottom of the oxide film [1,2]. The pore diameter and the film thickness can be controlled by the manufacturing conditions: the pore diameter ranges from a few ångström up to a few hundred ångströms, whereas the film thickness can reach tens of micrometer [2].

In order to bring catalytically active species on the alumina carrier, the anodised bodies must be immersed in solutions containing the desired metal salts or complexes. Depending on the pH value of the precursor solutions, some difficulties related to this approach may arise. Acid or basic solutions (outside the pH range 4.5–7.5 [7]) can leach the alumina film from the metal core. By using precursor solutions inside the mentioned pH range, the driving force for the immobilisation of the ionic species on the surface of alumina decreases strongly (the isoelectric point of alumina is in the range of pH 6.1–6.7 [8]), which results in relatively low loading and

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inhomogeneous distribution of the active species along the pores.

It was therefore the aim of the present work to develop a method for the production of shell-type metal-oxide-on-metal catalysts having regular pores, by incorporating the active component in the high surface oxide layer already during anodisation. The carriers were prepared by the ANOF technique (anodic oxidation by spark discharge [9]). In this technique, the oxide formation takes place by applying an intense electric discharge on the metal surface acting as anode; the surface metal melts and at the same time is oxidised, forming characteristic textures consisting of regular pores. By the appropriate selection of the electrolyte, active phase precursor, stabiliser and working conditions (potential, current density, frequency of pulses, time) oxide layers of different thickness (5–50 μm) and pore density ($1–3 \times 10^5$ pores/cm^2) containing the active component were obtained. The carriers used for anodisation were aluminium, titanium and magnesium. The active component precursors were salts of nickel, chromium or molybdenum. The catalysts were characterised with respect to the pore texture and distribution of the active component in the oxide layer. Selected catalyst samples were tested in the oxidative dehydrogenation of cyclohexane.

2. Experimental

Aluminium, titanium and magnesium wires (1 mm diameter) were employed as starting materials. The aqueous electrolyte solutions contained KH_2PO_4, $NH_4(H_2PO_4)$ and Na_2CO_3 as well as the precursors of the catalytically active component ($Ni(CH_3COO)_2$, $(NH_4)_2CrO_4$, $(NH_4)_6Mo_7O_{24}$, $Li(CH_3COO)$). A detailed description of the preparation method is given in [10]. The oxidised bodies were subsequently washed with distilled water and calcined at 600°C for 6 h. The wires were then cut into pieces of 4 mm length.

The catalysts were examined by scanning electron microscopy (SEM) to observe the pore structure. The concentration profiles of the chemical elements along the oxide film were determined by energy-dispersive X-ray spectroscopy (EDX) by using sectioned samples. The surface areas of the catalysts were measured by nitrogen adsorption following the BET method.

The catalytic tests were carried out in a conventional steady-state integral reactor at 450°C and at space velocities in the range 3–63 l/(g h) obtained by varying the catalyst amount at a constant flow rate of 15.9 l gas/h (NTP). The feeding mixture contained 0.2 vol.% cyclohexane in air and was prepared by mixing synthetic air and nitrogen saturated with cyclohexane. The analysis of the feed and effluent was performed on-line by using a gas chromatograph (HP 5890, FID detection) for the organic products, and an infrared photometer (BINOS, Fischer-Rosemount) for CO and CO_2.

3. Results and discussion

The catalysts prepared are listed in Table 1 together with some of their characteristics. The surface areas of the catalysts related to their total masses

Table 1
Denomination and characteristic data of the shell catalysts

Catalyst denomination	Constituent elements		Layer thickness (μm)	Surface area (m^2/g)[a]
	The oxide layer	The metal substrate		
Al	Al, O, P	Al	~3	Not determined
NiAl	Ni, Al, O, P	Al	15–19	0.4
NiTi	Ni, Ti, O, P	Ti	25–28	0.5
NiMg	Ni, Mg, O, P	Mg	16–23	0.3
NiLiAl	Ni, Li, Al, O, P	Al	~22	0.6
CrAl	Cr, Al, O, P	Al	14–17	0.6
MoAl	Mo, Al, O, P	Al	16–18	0.7

[a] The surface area is related to the total amount (catalyst + metal carrier).

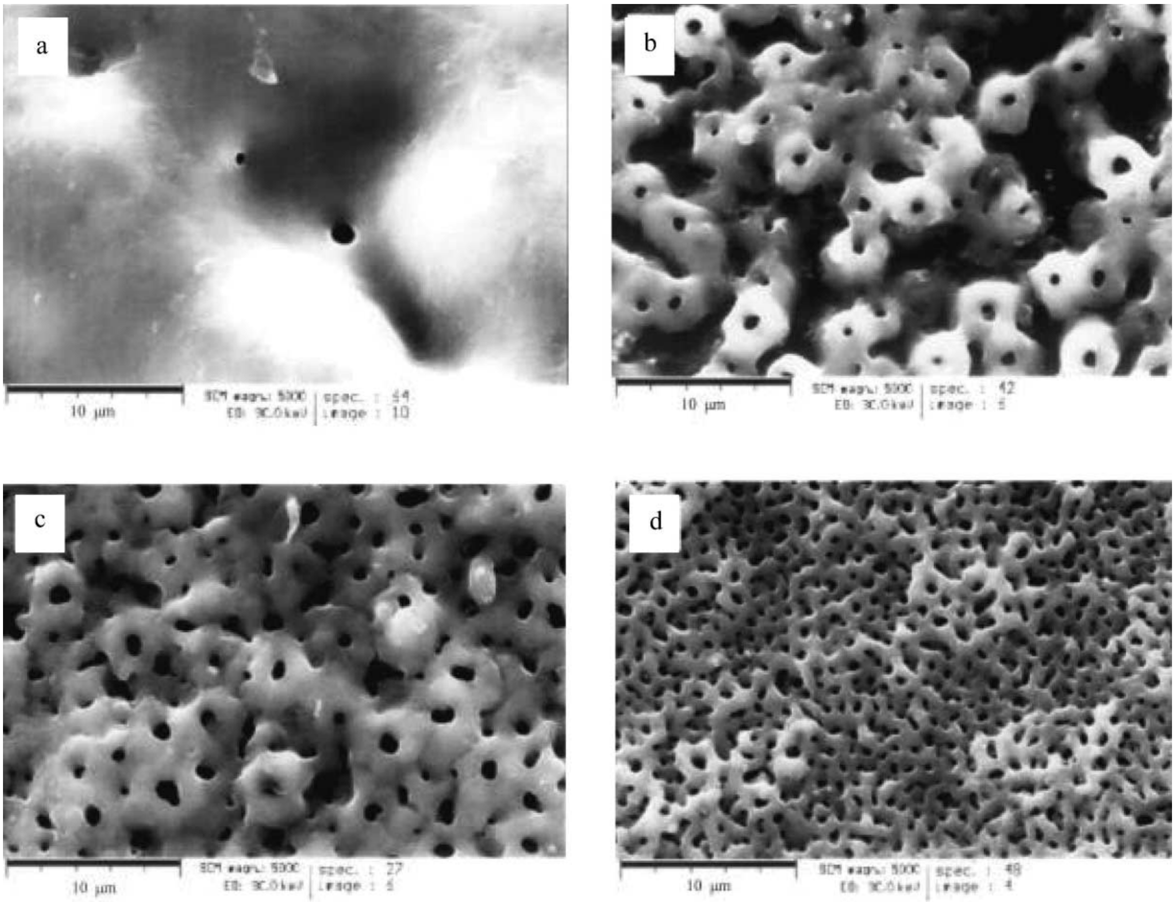

Fig. 1. SEM micrographs of anodic alumina films prepared in: (a) basic electrolyte mixture containing KH_2PO_4, $NH_4(H_2PO_4)$ and Na_2CO_3; (b) electrolyte (a) + $Ni(CH_3COO)_2$; (c) electrolyte (a) + $(NH_4)_2CrO_4$; (d) electrolyte (a) + $(NH_4)_6Mo_7O_{24}$.

(catalyst + metal support) are relatively low, because of the small thickness of the oxide film (between 14 and 26 µm) as compared to the wire diameter; they ranged between 0.3 m^2/g (nickel on magnesia) and 0.7 m^2/g (molybdenum on alumina). By examining the data of Table 1, it appears that the surface area related to the catalyst mass is not proportional with the layer thickness; for example, nickel supported on alumina and magnesia have the same thickness, but their surface areas differ. Moreover, chromium and molybdenum supported on alumina have thin layers, yet their surface areas are high. The surface area depends on the pore density, as the SEM micrographs show (Fig. 1). The catalysts containing Ni, Cr or Mo on alumina have pores with more regular and defined structure than the alumina anodised only in the presence of K, Na and NH_4 salts (Fig. 1a–d). Previous studies have shown that the formation and pore structure of the oxide film is influenced not only by the substrate metal and the type and size of the electric field applied to the electrodes (direct, alternating or pulsatory current), but also by the composition of the electrolyte solution used [9]. As seen in Fig. 1a, the alumina prepared by the ANOF technique in the presence of a mixture of electrolytes containing only potassium and sodium displays a low density of large and irregular pores, which makes it inappropriate as a catalyst carrier. The presence

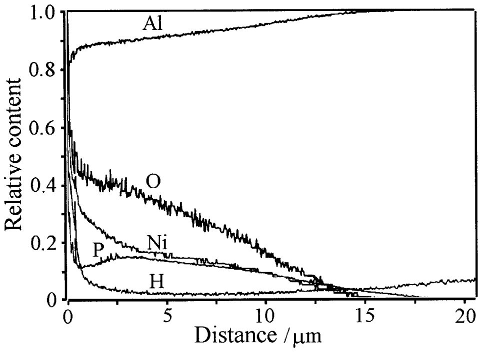

Fig. 2. Concentration profiles of chemical elements along the depth of the oxide film over the nickel/alumina/aluminium catalyst. The concentration ranges displayed are 0–100 wt.% for Al, 0–20 wt.% for O, 0–10 wt.% for Ni and 0–5 wt.% for P. The point zero on the X-axis represents the top of the oxide layer.

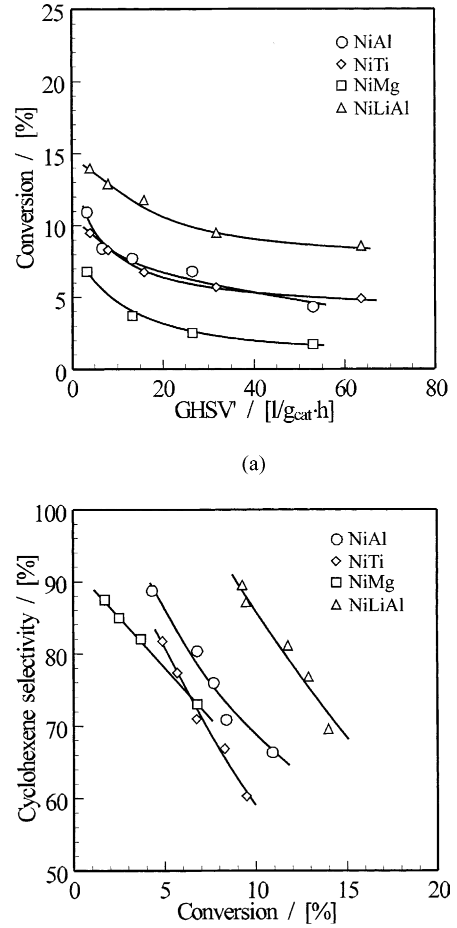

Fig. 3. Cyclohexane oxidation at 450°C over nickel-containing shell catalysts: (a) conversion grades as a function of the space velocity; (b) selectivity as a function of conversion.

of transition metal salts in the electrolyte solution provides not only a catalyst loaded with the active component, but improves the pore texture and enhances the pore density of metal oxide carrier (Fig. 1b–d). The pores diameter lay in the range of 0.2–0.8 μm and their lengths correspond approximately to the thickness of the oxide layers. The pore density amounts to 1–3 × 10^5 pores/cm^2 [9].

An example for the distribution of the chemical elements in the oxide layer is presented in Fig. 2 for nickel on alumina. The nickel concentration decreases from about 7 wt.% at the pore mouth to 2 wt.% in the first 3 μm of layer thickness, then remains constant along the pore length and drop to zero at the bottom of the layer. The concentration and distribution of the active component in the oxide layer can be controlled by the anodisation conditions [9,10].

Catalytic tests of cyclohexane oxydehydrogenation over the nickel-containing catalysts are presented in Fig. 3. At 450°C and space velocities of 3–63 l/(g h), the conversions of cyclohexane amounted to 2–7% over nickel/magnesia, 6–9.5% over nickel/titania and 5–11% over nickel/alumina. The lithium addition to the nickel/alumina catalyst enhanced the activity up to conversions of 10–14%. The low conversion levels originate probably from the low surface areas of the shell catalysts. Previous studies have shown that in the same operation range, the nickel catalysts supported on powder carriers (γ-Al_2O_3, 100 m^2/g and MgO, 26 m^2/g) yielded conversions of 30–60% (nickel on alumina) and 20–35% (nickel on magnesia) [11].

The oxidation of cyclohexane over nickel-containing catalysts yielded fairly high selectivity (between 60 and 90%) for cyclohexene (Fig. 3b). For comparison, the cyclohexene selectivity over the powder catalysts was in the range 5–30% (nickel on alumina) and 1–35% (nickel on magnesia). This finding shows the potential of the shell catalysts with regular pores for the industrial manufacture of the cyclohexene. Other products were 1,3-cyclohexadiene (selectivity of 3–5%), benzene (15–24%) and carbon oxides. The addition of lithium provides, besides the improvement of activity, also an enhancement of cyclohexene selectivity with about 10–20%.

4. Conclusion

The anodic oxidation by spark discharge of metal substrates in the presence of aqueous electrolyte solutions yielded the corresponding oxides in the form of thin porous films supported on the metal core. When the anodisation process was carried up in a solution containing cations of various transition metals, they were incorporated in the anodic oxide and yielded supported catalysts with regular pore systems directed towards the metal core of the substrates. The nickel catalysts supported on alumina, magnesia or titania were found to be selective in cyclohexane oxydehydrogenation to cyclohexene. Their catalytic behaviour suggests that the use of carriers with regular open and short pores is of advantage for the improvement of cyclohexene selectivity as compared to classical powder catalysts by favouring the rapid transportation of the intermediate from the active surface of the catalyst.

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