

REDUCTION OF SULPHATE CONTENT FROM COATED ALUMINA $SO_4^{2-}/Al_2O_3/Al$ (OXIDE LAYER) BY HYDROGEN SPILLOVER

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ABSTRACT

Coated metal catalysts find wide industrial applications. The problem of these catalysts are low adhesion strength of the coat on the support, non uniform thickness of the coat and the irregular pore system. Much effort has been devoted in recent years by manufacturing new coated catalysts in order to improve the adverse effect. Among this was manufacturing of porous coated catalyst through anodic oxidation. The only problem of such catalysts was the high content of anion from the electrolyte which is incorporated into the oxide layer during the anodic oxidation. The aim of this study was to reduce the anion (sulphate) content from such oxide layer using spillover phenomena. Three catalysts were used for this purpose as a spillover hydrogen generator. From the three used catalysts Pd/Al_2O_3 is the only catalyst that can reduce anion from this oxide layer. The result showed the possibility of hydrogen spillover to reduce the anion content from coated catalyst. An introduction to spillover phenomena is also given first to enhance the capacity of the reader.

INTRODUCTION

At present, about 90% of industrial organic synthesis are carried out through the use of catalysts. The formation of maleic anhydride by selective oxidation of

benzene as well as selective oxidation of o-xylene to phthalic anhydride are a few examples. Since a catalytic reaction occurs at the fluid-solid interface a large interfacial area can be helpful in attaining high reaction rate. In many catalysts, this area is provided by porous structure. A catalyst that has a large area resulting from pores is called a porous (conventional) catalyst. There are two types of porous catalyst, namely bulk & coated (supported) catalyst.

Conventional bulk catalysts (Fig. 1(a)) have irregular pore system with a long diffusion path which followed during reaction of unwanted side production. Conventional coated catalysts (Fig. 1(b)) consist of an inert unporous support e.g. Al_2O_3 , which bears the catalytically active component e.g. V_2O_5 (porous oxide) as shell or coat. These catalysts have shorter diffusion path and as a consequence, the formation of unwanted side production is lower than in the corresponding reaction catalyzed by bulk catalysts. Major disadvantages are low adhesion strength of the coat on the support, nonuniform thickness of the coat and the irregular pore system.

To overcome these problems, a novel type of coated catalyst such as in Fig. 1(c) have been the subject of intense study in the past [1-3]. In the last few years, our team has put a lot of effort to develop a novel type of coated catalyst (oxide layer) through anodic oxidation of aluminum wire [4-6].



Figure 1 Mode of catalysts; a) conventional bulk catalyst, b) conventional coated catalyst, c) anodic coated catalyst; 1-catalytically active components, 2-pore, 3-porous oxide, 4-nonporous Al_2O_3 layer, 5-supporter, 6-not-oxidized Aluminium wire

The anodic oxidation of aluminum wire gives: a regular pore structure with unbranched cylindrical pores, equal pore lengths and as well as equal distance between the pore [7]. This leads to the assumption that the uniform pore system allows shorter path to the molecules as a result of high selectivity to the wanted product. Furthermore, the oxide layer adheres strongly to the aluminium core [Fig. 2].

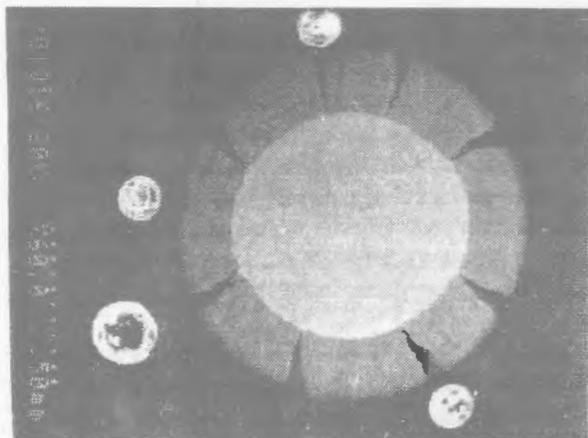


Figure 2 Cross-sectional view of anodic coated catalyst

The anodic oxidation of aluminium wire is carried out either in diluted acids or in organic solutions. Characteristics measurements indicated that the product of electrolysis was not in pure layer of alumina (Al_2O_3) but a form of anion incorporated into the oxide layer ($SO_4^{2-} \cdot Al_2O_3 / Al$) as shown in the schematic model of Fig. 3. In our experiment, anodic oxidation of aluminium wire (99.99%), with 20% H_2SO_4 , with 20V dc current, at 25°C gave 30 wt.% sulphate which is incorporated into the oxide layer during anodic oxidation as a form of $SO_4^{2-} \cdot Al_2O_3 / Al$. Such big amounts of anion content might reduce the capacity to take sufficient foreign active agent during impregnation. Accordingly, the aim of this work was to reduce the anion (sulphate) content from oxide layer ($SO_4^{2-} \cdot Al_2O_3 / Al$) by using the spillover phenomena.

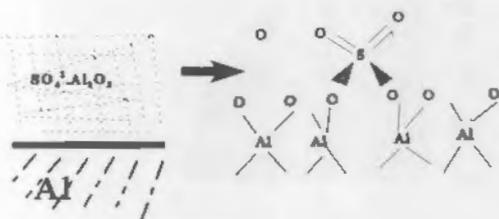


Figure 3 A schematic models of $SO_4^{2-} Al_2O_3 / Al$

THE SPILLOVER PHENOMENA

Although the phenomena of hydrogen spillover was first noticed in the 1950's [8] up to now the spillover phenomena is still controversial, which underline the need for explanation.

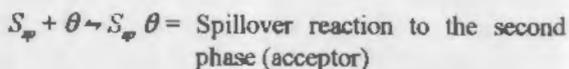
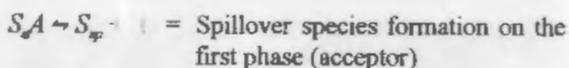
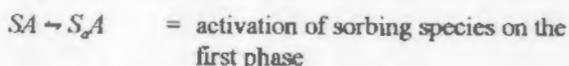
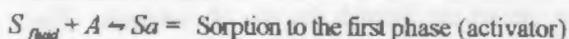
In the First International Symposium on the Spillover of Adsorbed Species (FISSAS) in 1982 was proposed a definition of spillover [9]:

Spillover involves the transport of an active species sorbed or formed on a first phase onto another phase that does not under the same condition sorb or form the species.

The FISSAS offered as a comment: the result may be the reaction of this species on the second phase with other sorbing gases and /or reaction with, and/or activation of the second phase.

To simplify the definition, a species is absorbed from the gas phase onto a metal (activator) where it dissociates atomic species. Spillover occurs if the atomic species is then able to migrate across the surface to the acceptor (metal, oxide, etc). Figure 4 represents the two combination cases where spillover may occur. Migration over a distance from the primary source to acceptor was detected by a sufficient number of authors [10]. The atomic species created by spillover may be an ionic (H^+), a radical (H^\cdot) or a bonded species ($H-$) [11].

The spillover phenomena can be interpreted using the following mechanical sequence:



Where S_{fluid} = the species sorbing from the fluid (gas or liquid)

A = the site able to adsorb/ desorb (activator)

S_a = activated sorbed species

S_{sp} = spiltover species

θ = acceptor

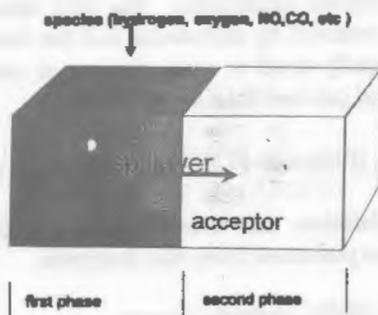


Figure 4 Schematic representation of spillover phenomena

It is generally accepted that spillover depends on at least two prerequisites:

- i) A primary source (activator) for the splitting species, such as metal of group VIII (e.g. Pd, Pt), support catalysts (e.g. Pt/Al₂O₃, Pd/Al₂O₃) and oxides (e.g. Fe₂O₄)
- ii) A secondary source (acceptor) for taking species

The primary source & acceptor are formulated through one of the following combinations:

- a) Physical mixing
- b) Impregnation of oxide with metal compound (supported catalyst e.g. Pt/WO₃)
- c) Impregnation of oxide with supported catalyst (e.g. MoO₃/Pt/Al₂O₃)

Figure 5 shows schematically the way on how the primary source and acceptor are formulated. Factors influencing the spillover can be noticed among the literature data. The following is a list of these factors: the range of temperatures of adsorption; the amount & percentage dispersion of the primary source; the nature of the contact between the primary source and the acceptor; the specific surface areas of the coupled primary source-acceptor; the role of the partial pressure of sorbed species; the strength of the bond between split-over species and acceptor sites; the chemical nature of the acceptor & source; and the duration of chemisorption.

Literature data give evidence for spillover occurring on group VIII, VI and I metal (mono or bimetallic system) supported on refractory inorganic oxides such as Al₂O₃, SiO₂, zeolites or carbons. It is assumed that the

group metals were able to chemisorb gases such as hydrogen [12-13].

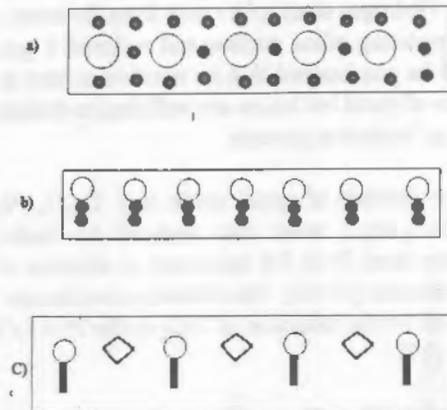


Figure 5 Schematic way of formulation for spillover reaction; metal (○), acceptor (●), oxide (◇), supporter (■); a) physical mixing, b-c) impregnation of activator with acceptor

The split-over species may:

- i) exchange with similar surface species
- ii) react with the surface ($H_{sp} + MOM^* \rightarrow M-OH + M^*$) which can result in the creation of surface active and/or defects sites (catalytically)
- iii) transform the bulk of the solid into a different structure.

For the sake of clarity a few consequences of spillover are summarized below:

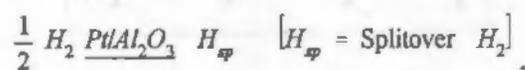
Dehydration of cyclohexane to benzene is carried out in the presence of Pt (0.5%) / Al₂O₃ catalyst admixed with pure Al₂O₃. The hydrogen passed to the reactor is adsorbed on Pt/Al₂O₃ and form hydrogen atom. The hydrogen atoms split-over from Pt to the pure Al₂O₃ and dehydrogenation of cyclohexane to benzene occurs according to mechanism [11]:



The reaction has shown inactive in the presence of pure Al₂O₃.

Spillover hydrogen was observed by Van Meerbeek et al. [14] to reduce the surface of silica gel containing only traces of metals Ni, Pd, Pt, Ta and W. The reaction was carried out in the Pyrex reactor in the presence of 60 Torr H_2 at about 880°C. Hydrogen is adsorbed/desorbed by forming hydrogen atom on the metal. Hydrogen atom split - over from the metal onto its supporting silica surface and reduced it gel. It should be emphasized that no reaction occurs in the absence of metal but traces are sufficient to initiate the silica gel reduction process.

A large number of metal oxide (e.g. Co_3O_4 , V_2O_5 , WO_3 , TiO_2 etc.) were also reduced by hydrogen spillover from Pt or Pd supported on alumina or on silica -alumina [15-16]. The following mechanism was observed by the reduction of TiO_2 on the Pt/ Al_2O_3 at 875°C [17].



Substantial experimental evidence has been found for the spillover of hydrogen species. Hydrogen is not, however, the only species which can split - over from the primary source to the acceptor. At the present time, the spillover of oxygen, carbon monoxide, isocyanate & various organic radicals have been detected [18-21].

EXPERIMENTAL

Materials Preparation

A) $SO_4^{2-} \cdot Al_2O_3/Al$ (Oxide layer)

An extensive description of techniques used in the preparation and after treatment of $SO_4^{2-} \cdot Al_2O_3/Al$ had been provided in [4 - 6]. The $SO_4^{2-} \cdot Al_2O_3/Al$ was prepared from aluminum wire (99.999%) through anodic oxidation. The wire was mounted on a special anod hanger and anodized in 20% H_2SO_4 at 25°C with constant direct voltage of 16.5 V for 2 hrs. Aluminum sheets were used as counter electrode. Fig. 2 depicts cross-section of $SO_4^{2-} \cdot Al_2O_3/Al$. The anodized wire $SO_4^{2-} \cdot Al_2O_3/Al$ dried at 120°C for 2 hrs and calcined at 450°C for 6 hrs. The oxide layer cut into rods of 5mm length.

B) Pd/ γ - Al_2O_3

66 mg palladium (II) - acetate [$Pd(CH_3COO)_2$] was dissolved in 30 ml of methanol. The solution were then added to 1.64g of γ - Al_2O_3 . The suspension was

shaken for a long time and kept for two days to reach complete adsorption equilibrium. The clear excess solution was removed by decantation and the residu (Pd/Al_2O_3) finally dried in pure nitrogen at room temperature and calcined for 6 hrs at 450°C.

C) Pt/ Al_2O_3 [Platinum (0.5%) on Alumina]

The solid platinum on alumina used for this experiment was purchased from Alfa Inorganic.

D) Soaked - Pb(II) - Acetate. - paper

This was used as an indicator method for liberation of H_2S . White paper was immersed in a saturated solution of lead acetate at ambient temperature. The soaked - lead - acetate - paper was dried then in oven at 110°C.

Method

Equal amount of materials were subsequently charged into the reactor for reduction of sulphate from $SO_4^{2-} \cdot Al_2O_3/Al$ in the following sequences:

- Experiment No. 1 $SO_4^{2-} \cdot Al_2O_3/Al$ (4 g)
 " " 2 Equal amount (2 g each) of
 $SO_4^{2-} \cdot Al_2O_3/Al$ & Pd/Al_2O_3
 (physically mixed)
 " " 3 Equal amount (2 g each) of
 $SO_4^{2-} \cdot Al_2O_3/Al$ & Pt/Al_2O_3
 (physically mixed)

The materials were heated in the reactor over night in flowing nitrogen at 450°C to avoid any alteration during the experiments due to sintering. The reduction of sulphate was studied at atmospheric pressure in the temperature interval of 50°C and range of 350 - 500°C. At each of these points with interval of 10 hrs the sulphate content and the specific surface area of the materials were measured.

Apparatus

The three experiment were performed in a flow type apparatus operated at atmospheric pressure [fig 6]. Due to the nature of reaction with hydrogen, the apparatus were washed with nitrogen before beginning the investigation experiment and kept under nitrogen atmosphere at 300°C when not in use. Nitrogen was passed through drying column 1 (filled with P_2O_5). By changing the three - ways valve (H_1) hydrogen was entered into the fixed bed reactor 2. The fixed bed reactor was filled according to the method described

above. The reactor has been preheated in nitrogen at 400°C for 2 hrs and maintained experimental temperature of 350-, 400-, 450 - and 500°C. To detect the emission of H₂S, soaked Pd (II)-Acetate - paper were hanged in glass tubes 3 from time to time the soaked paper was changed without breaking the reaction using three - way - valves H₂ and H₃. The effluent gas was controlled using a trap 4 filled with water. With time interval rods of SO₄²⁻. Al₂O₃/Al were taken from the fixed bed reactor and a sulphate content and surface area were analyzed.

RESULTS & CONCLUSION

For the whole experiment, the white soaked paper of Pb (II) - acetate hanged in a glass tube of the apparatus has shown no change of colour as a result of emission of H₂S in the range 350- 400°C for 80 hrs. Even raising the temperature to 500°C, the soaked paper remained without change of colour for the experiment numbers 1 and 3. The measurement of sulphate content was also proved and showed no change to the previous condition. In contradiction to this, the

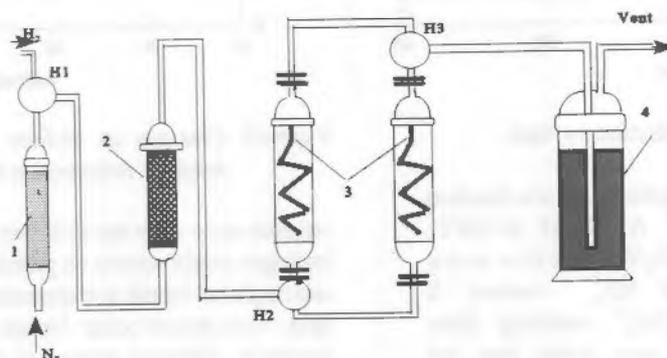


Figure 6 Schematic diagram of apparatus : 1. V₂O₅ trap, 2. Fixed bed reactor, 3. Soaked lead acetate paper, 4. Water trap, H1, H2, H3 - three ways valve

Analytical Method

Sulphate Content

The sulphate content of SO₄²⁻. Al₂O₃/Al was obtained by the line - scan using Energy Dispersive X - ray analysis (EDX) [Tracor, SN 4200]

Specific Surface Area

Surface area of SO₄²⁻. Al₂O₃ /Al was determined by nitrogen gas adsorption at 77 K according to the convenient BET method with the help of Micro metric Accusorb 2100E.

amount of sulphate left in the experiment 2 decreased most drastically from 30 wt.% to 4 wt.% at 450°C and 500°C in 80 hrs. The surface area was changed from 8.7 m²/g to 11.3 m²/g.

Table 1 shows the observed sulphate and surface area for the experiment 2 at 450°C. Figure 7 shows again the sulphate content as a function of time for experiment 2. In the initial period of the run, the sulphate content decreased rash from 30 wt.% to 19.6 wt.% (about 34%) with 10 hrs. Increasing the time to 80 hrs gave only 50.8%.

Table 1: Experimental results of coated SO₄²⁻. Al₂O₃/Al at 450°C.

Experiment No.	Before Exp.		After Exp.	
	SO ₄ ²⁻ /Wt.%	S _{BET} /M ² /g	SO ₄ ²⁻ /Wt.%	S _{BET} /M ² /g
1	30	8.7	30	8.7
2	30	8.7	4.2	11.3
3	30	8.7	30	8.7

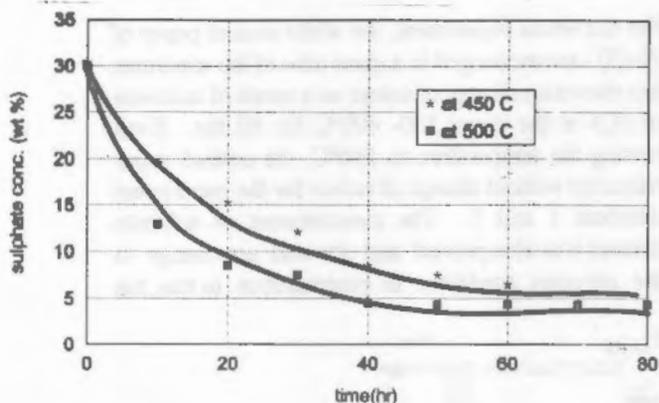


Figure 7 Sulphate reduction vs. time

Figure 8 shows the result of surface area as a function of SO_4^{2-} content over $SO_4^{2-} \cdot Al_2O_3/Al$ at 450°C. Here, S_{BET} of $SO_4^{2-} \cdot Al_2O_3/Al$ decreases progressively with increase of SO_4^{2-} content. It seems that the liberated SO_4^{2-} resulting from spillover hydrogen created new pores that are responsible for the observed increase in the S_{BET} of $SO_4^{2-} \cdot Al_2O_3/Al$.

The dramatic difference between pure $SO_4^{2-} \cdot Al_2O_3/Al$ (exp. 1) and mixture of $SO_4^{2-} \cdot Al_2O_3/Al$ with Pd/Al_2O_3 is evident from the qualitative data in table 1. This table clearly shows the effect of Pd/Al_2O_3 on the rate of H_2 uptake, which adsorb/desorbs, migrate and react immediately with $SO_4^{2-} \cdot Al_2O_3/Al$. Consequently, the function of Pd is to provide a source of H atoms which spillover to $SO_4^{2-} \cdot Al_2O_3/Al$ and are responsible for sulphate reduction. It is widely accepted that H_2 is dissociatively adsorbed over Group VIII metals [22].

In comparing the finding of experiments 2 and 3, there is a general consensus that both Pd and Pt are spillover activators. However, spillover involves a sequence of steps and each of these steps may be influenced by the preparation and nature of materials. The reduction of

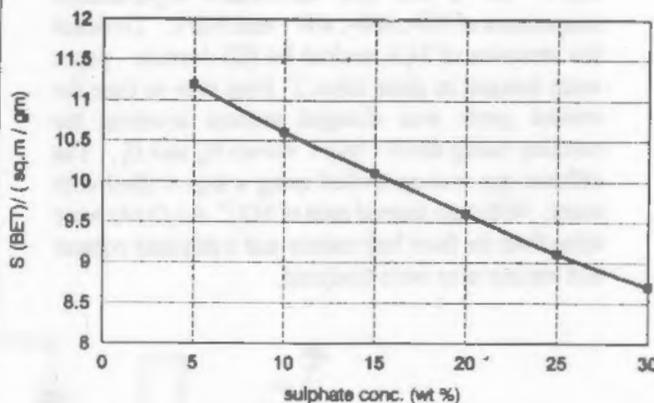
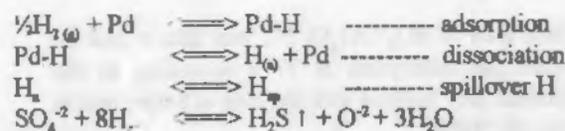


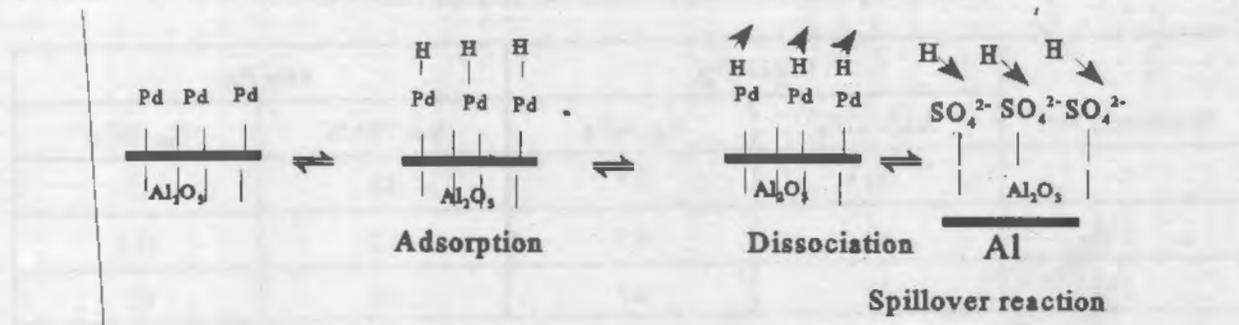
Figure 8 Changes in surface area as a result of sulphate reduction at 450 °c

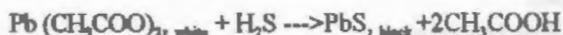
sulphate occur after the spillover process. In our case, hydrogen might adsorb on platinum (Pt/Al_2O_3 , exp.3) and might not desorb at experimental condition and the split-over did not occur. Hence spillover is necessary but not a sufficient process to induce the effects that have been found. This demonstrates that multi-effect nature of spillover. Unfortunately, detailed information on the nature of interaction between Pd and Pt on $SO_4^{2-} \cdot Al_2O_3/Al$ are difficult to derive in these experiments.

The reaction in the experiment 2 has proceeded through the following sequence of elementary steps. Adsorption/desorption of hydrogen on palladium, migration of hydrogen atom across the alumina surface to the coated $SO_4^{2-} \cdot Al_2O_3$ surface and reaction with SO_4^{2-} . The corresponding mechanism and schematic model could therefore be:



where: H_a ---- activated hydrogen
 H_{sp} --- spillover hydrogen



Indication reaction**CONCLUSION**

In conclusion, the result presented here shows that adsorbed hydrogen atoms formed on palladium are able to split - over onto alumina surface and diffuse to $\text{SO}_4^{2-} \cdot \text{Al}_2\text{O}_3/\text{Al}$. The reaction between spillover hydrogen and sulphate on the surface provided hydrogen sulphide which is exhibited as a black colour on the soaked- lead-acetate- paper. The reduction of sulphate from $\text{SO}_4^{2-} \cdot \text{Al}_2\text{O}_3/\text{Al}$ caused the enhancement of surface area and this effect might create new pores that will be filled latter by active species.

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