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CHARACTERIZATION OF HYDRODENITROGENATION CATALYSTS BY O_2 CHEMISORPTION

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O_2 chemisorption on sulfided $NiMo/Al_2O_3$ catalysts with $Ni/Ni + Mo = 0$ to 1 was measured at 273 K. The quantities of chemisorbed O_2 were compared to the activities of the catalysts in biphenyl hydrogenation and in 1,2,3,4-tetrahydroquinoline hydrodenitrogenation (HDN) at 623 K, 3.5 MPa.

1. Introduction

Several authors [1–4] have tried to establish relationships between the amount of chemisorbed O_2 and the activities of sulfided CoMo and NiMo catalysts in hydrodesulfurization and in hydrogenation. It is assumed that O_2 chemisorbs on sulfide anion vacancies which are supposed to be the catalytic centers for the reactions under consideration. It seems however that the sensitivity of O_2 chemisorption towards the promoting effect is not that obvious [2,3] and it depends in particular on the molybdenum content of the catalyst [4]. O_2 chemisorption was also used to characterize hydrodenitrogenation (HDN) catalysts [5,6]. It was found [6] that O_2 uptake by NiMo catalysts increased when their activity in HDN of a gasoil increased. However the authors concluded that O_2 adsorption was not selective towards the active sites of the reaction but rather was proportional to the total number of sites on the catalyst.

In this work, the amount of O_2 chemisorbed at 273 K was compared to the catalytic activities in the hydrogenation of biphenyl and in the HDN of 1,2,3,4-tetrahydroquinoline of $NiMo/Al_2O_3$ catalysts whose $Ni/Ni + Mo$ atomic ratio varied between 0 and 1.

2. Experimental

CATALYSTS

A series of $NiMo/Al_2O_3$ catalysts (table 1) with the same $Ni + Mo$ atomic concentration and with a $Ni/Ni + Mo$ atomic ratio varying from 0 to 1 were

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Table 1
Characterization of the catalysts

Ni/Ni + Mo	0	0.1	0.2	0.30	0.35	0.4	0.5	0.7	1
Ni (wt%)	–	0.88	1.76	4.4	3.06	3.54	4.40	6.13	8.80
Mo (wt%)	14.40	12.95	11.50	10.1	9.33	8.66	7.20	4.33	–
area (m^2g^{-1})	240	230	240	200	230	230	210	225	230

prepared by the pore filling method using nickel nitrate and ammonium heptamolybdate. The carrier was a γ-alumina (GFS, Rhône-Poulenc) with a BET surface area of 220 m^2g^{-1}. The molybdenum was introduced first, then after drying the sample at 393 K, the nickel. A commercial $NiMo/Al_2O_3$ catalyst (HR346, Procatalyse, $Ni/Ni + Mo = 0.3$) was used as a reference standard. Details concerning the characterization of the catalysts were given elsewhere [7].

CATALYTIC EXPERIMENTS

Biphenyl hydrogenation and 1,2,3,4-tetrahydroquinoline decomposition were carried out in a fixed bed microreactor at 623 K, 3.5 MPa with n-decane as solvent. Details concerning the procedure and the techniques were also reported elsewhere [7].

O_2 CHEMISORPTION

The catalyst sample (50 mg, oxide form) was dried in a flow of nitrogen (10 $cm^3.min^{-1}$) for 14 hours at 623 K. After cooling it down to room temperature, the nitrogen was replaced by the sulfiding mixture (10% H_2S in H_2, 10 $cm^3.min^{-1}$) and the temperature was raised at a rate of 5 $K.min^{-1}$ from ambient to 573 K. This temperature was maintained for 4 hours. The system was then cooled down to 273 K, swept with ultrapure argon (N60, Air Liquide; O_2 plus H_2O impurities < 1 ppm) and pulses of O_2 (0.244 cm^3) were injected every minute till saturation was obtained. The amount of chemisorbed $O_2(O_c)$ was calculated by the equation.

$$O_c(\text{mol}.O_2) = N_p\left(n - \frac{\Sigma h_i}{h_M}\right)$$

where N_p is the number of mol of O_2 in a pulse, n, the number of pulses, h_i, the peak height corresponding to the non-retained O_2 in injection number i, h_M, the peak height corresponding to O_2 at saturation.

3. Results and discussion

Figure 1 shows the amount of O_2 chemisorbed at 273 K (corrected from the amount retained by the alumina carrier at the same temperature) as a function of

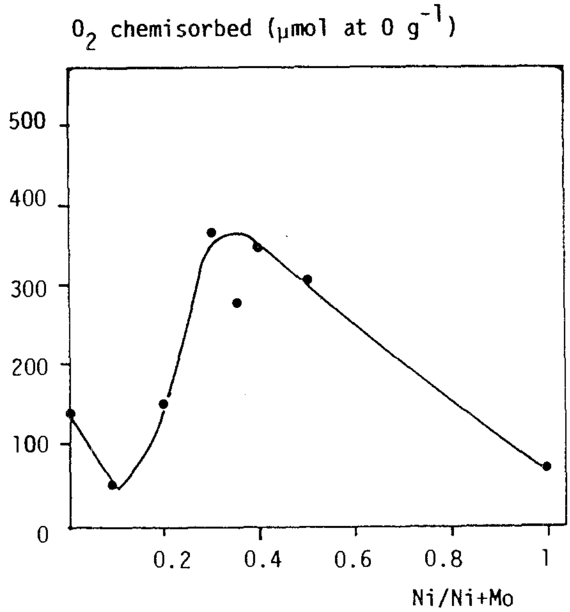
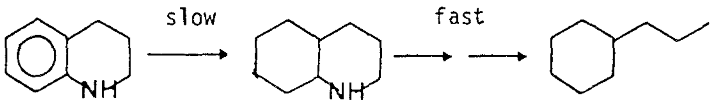


Fig. 1. Amount of O_2 chemisorbed at 273 K on $NiMo/Al_2O_3$ catalysts as a function of the Ni/Ni + Mo atomic ratio.

the atomic ratio of Ni/Ni + Mo. A maximum of the O_2 uptake is obtained with catalyst with a Ni/Ni + Mo ratio between 0.3 and 0.4. This corresponds to the maximum in activity in hydrodenitrogenation, namely, the formation of propylcyclohexane from 1,2,3,4-tetrahydroquinoline [7]. However, the correlation between the catalytic activity and the amount of chemisorbed O_2 is not very good (fig. 2). In particular, the quantity of O_2 chemisorbed on the unpromoted molybdenum catalyst and on the pure supported nickel catalyst compared to their catalytic activity is too high. Nevertheless the correlation between the amount of O_2 chemisorbed and the activity of the catalysts in HDN is quite similar to the one between the amount of O_2 chemisorbed and the activity in biphenyl hydrogenation (fig. 2). This can be explained by the fact that under the conditions of the HDN of 1,2,3,4-tetrahydroquinoline, the rate-limiting step of the formation of propylcyclohexane is the hydrogenation of the benzenic ring [7,8].



Both reactions (hydrogenation of biphenyl and formation of propylcyclohexane from 1,2,3,4-tetrahydroquinoline) which show a significant promoting effect would occur preferentially on nickel containing catalytic centers. The weak correlation and especially the fact that the unpromoted catalyst chemisorbs a

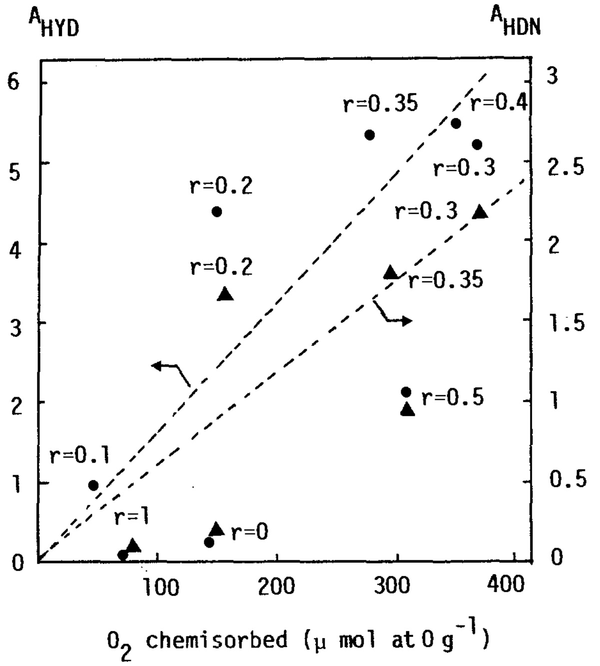
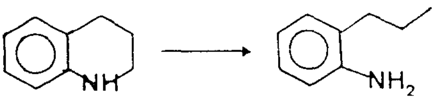


Fig. 2. Relationship between the activity of NiMo/Al_2O_3 catalysts in HDN (propylcyclohexane formation from 1,2,3,4-tetrahydroquinoline, 623 K, 3.5 PMa) and in biphenyl hydrogenation (623 K, 3.5 MPa) and the quantity of O_2 chemisorbed at 273 K. A_{HDN}: activity in HDN ($mmol.h^{-1}.g^{-1}$, ▲); A_{HYD}: activity in biphenyl hydrogenation ($mmol.h^{-1}.g^{-1}$, ●); r = Ni/Ni + Mo atomic ratio.

large amount of O_2 could indicate that oxygen chemisorbs on every vacancy, promoted or not by nickel. This is quite in agreement with the conclusions of Millman et al. [6]. On the other hand, a much better correlation is observed (fig. 3) between the amount of O_2 chemisorbed and the activity in the formation of orthopropylaniline from 1,2,3,4-tetrahydroquinoline:



which does not involve a hydrogenation step and for which a much lower promoting effect was observed [7]. This can be interpreted by supposing that this reaction can occur both on promoted and on unpromoted vacancies, both types being able to absorb oxygen.

The theory that C-N bond cleavage could occur on all the sites capable of adsorbing O_2 whereas the hydrogenation of aromatic rings would occur preferentially on promoted centers is also supported by the effect of H_2S on the activity in hydrogenation and in C-N bond cleavage of NiMo catalysts [8–14]. Actually, the presence of H_2S promotes more C-N bond cleavage than it inhibits hydrogenation. This again can be interpreted by assuming that all the sites capable of

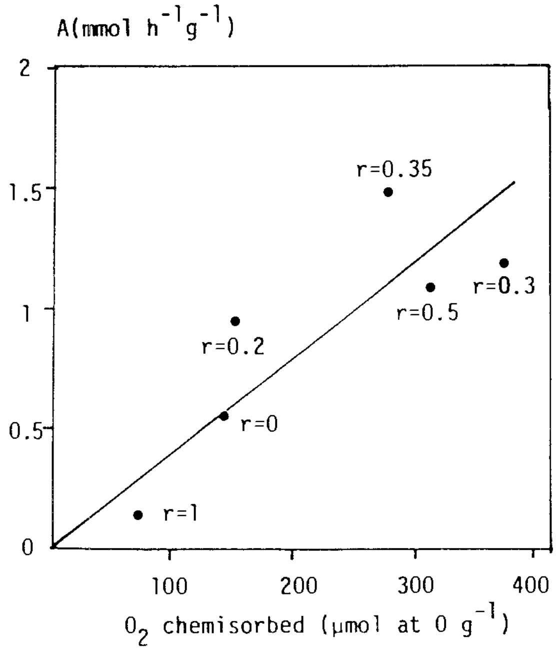


Fig. 3. Relationship between the activity of NiMo/Al_2O_3 catalysts in orthopropylaniline formation from 1,2,3,4-tetrahydroquinoline (623 K, 3.5 MPa) and the quantity of O_2 chemisorbed at 273 K. r = Ni/Ni + Mo atomic ratio.

adsorbing H_2S (or O_2) would catalyze C-N bond cleavage whereas the hydrogenation of aromatic rings would occur preferentially on a fraction of them.

References

[1] B.M. Reddy and V.S. Subramanian, Appl. Catal. 27 (1986) 1.
[2] W. Zmierczak, G. Muralidhar and F.E. Massoth, J. Catal. 77 (1982) 432.
[3] R. Burch and A. Collins, Appl. Catal. 17 (1985) 273.
[4] J. Bachelier, J.C. Duchet and D. Cornet, J. Catal. 87 (1984) 283.
[5] T.A. Bodrero and C.H. Bartholomew, J. Catal. 84 (1983) 145.
[6] W.S. Millman, C.H. Bartholomew and R.L. Richardson, J. Catal. 90 (1984) 10.
[7] G. Pérot, S. Brunet and N. Hamzé, 9th Intern. Congress Catalysis, Calgary 1988, accepted for publication.
[8] G. Pérot, S. Brunet, C. Canaff and H. Toulhoat, Bull. Soc. Chim. Belg. 96 (1987) 865.
[9] C.N. Satterfield and S. Gültekin, Ind. Eng. Chem. Process Des. Dev. 20 (1981) 62.
[10] S.H. Yang and C.N. Satterfield, J. Catal. 81 (1983) 168.
[11] S.H. Yang and C.N. Satterfield, Ind. Eng. Chem. Process Des. Dev. 23 (1984) 20.
[12] A. Olalde and G. Pérot, Appl. Catal. 13 (1985) 373.
[13] S. Brunet and G. Pérot, React. Kinet. Catal. Lett. 29 (1985) 15.
[14] C.N. Satterfield, G.M. Smith and M. Ingalls, Ind. Eng. Chem. Process Des. Dev. 24 (1985) 1000.