

Hydrodeoxygenation of Furan: Characterization of Promoted and Unpromoted Tungsten Sulphide Catalysts by Low Temperature Oxygen Chemisorption and its Correlation with Hydrodeoxygenation

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The amount of oxygen chemisorbed at -78°C has been measured on the sulphided surface of tungsten catalysts supported on Al_2O_3 and SiO_2 ; it is shown for the first time that there is a correlation with the activity of the catalyst for hydrodeoxygenation of furan.

Hydrodeoxygenation of oxygen-containing compounds in synthetic oils derived from coal, shale, and other products is receiving increasing interest. Aromatic ethers and single-ring phenols are the major constituents of the oxygenated compounds.^{1,2} Catalytic hydrotreatment is generally carried out at elevated temperatures in the presence of CoMo and NiMo catalysts.^{3,9-11} For the first time a systematic investigation has been undertaken of the applicability of low temperature oxygen chemisorption (LTOC) and its correlation with hydrodeoxygenation (HDO) activity on catalysts promoted with nickel and cobalt and unpromoted tungsten on Al_2O_3 and SiO_2 supports.

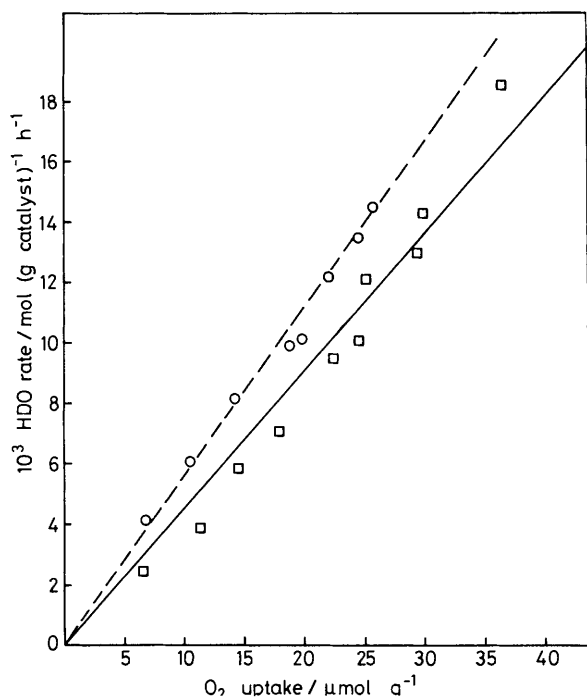
LTOC is a powerful tool for characterizing supported molybdenum oxide and sulphide and vanadium oxides.³⁻⁸ It has been found that LTOC data correlate directly with the hydrodesulphurization (HDS) and hydrogenation (HYD) activities of Mo-based hydroprocessing catalysts.⁹⁻¹¹

However, similar studies with supported tungsten catalysts have not yet been reported. We now report a correlation between oxygen uptake capacity (at -78°C) of two series of promoted and unpromoted tungsten catalysts and HDO of furan.

The experimental procedure for the preparation of the catalysts has been given elsewhere.⁵⁻⁷ Catalysts containing up to 25% of W (w/w) were prepared by the well established wet-impregnation technique and promoted catalysts were prepared by the double impregnation of 19% W on both supports. Oxygen chemisorption was performed at -78°C on the catalysts presulphided using a mixture of CS_2 and H_2 (flow rate 35 ml/min) at 400°C for 2 h. After sulphiding, the hydrogen gas flow was stopped and the catalyst cell, which is specially designed, was attached to a high vacuum system and evacuated at 400°C for 4 h. A flow microreactor, interfaced by a six-way gas sampling valve with a gas chromatograph, was

Table 1. Oxygen chemisorption and HDO rate on sulphided, promoted (with Ni and Co) tungsten catalysts supported on γ -Al₂O₃ and SiO₂.

W (%)	Catalyst composition		O ₂ chemisorption/ $\mu\text{mol g}^{-1}$		10^3 HDO rate/mol (g catalyst) ⁻¹ h ⁻¹	
	Co (%)	Ni (%)	γ -Al ₂ O ₃	SiO ₂	γ -Al ₂ O ₃	SiO ₂
19	1.0	—	18.74	10.2	18.39	14.23
19	3.0	—	32.12	16.06	25.36	20.29
19	5.0	—	37.92	20.07	31.10	29.35
19	—	1.0	21.41	15.16	18.72	21.13
19	—	3.0	35.24	21.42	45.64	36.60
19	—	5.0	39.71	29.00	64.72	50.70

**Figure 1.** Hydrodeoxygenation rate as a function of oxygen uptake at -78°C (corrected for oxygen uptake on pure supports). Measurements for unpromoted pre-sulphided tungsten catalysts supported on (□) Al₂O₃ and (○) SiO₂.

used to study the hydrodeoxygenation of furan at 400°C under differential conditions of reactor operation and in the absence of any mass transfer effect.

The HDO rate of furan by the catalysts is plotted as a function of oxygen uptake by the various catalysts in Figure 1. It is clear that there is a direct correlation between the HDO activity and the amount of oxygen chemisorbed at -78°C by the presulphided catalysts. It is generally believed that there is more than one type of active site on the surface of WS₂. The generally accepted mechanism is that co-ordinatively unsaturated sites (CUS), here W ions generated upon sulphiding, are the active sites for hydrogenation and hydrodesulphurization.^{5,6} Furthermore, oxygen when chemisorbed at -78°C does so dissociatively on the CUS. The linear correlation in Figure 1 indicates that HDO occurs on the same CUS on which HYD, HDS, and LTOC take place. HDO activity of the catalyst passes through a maximum at monolayer formation (20% w/w W on Al₂O₃ and 12% w/w W on SiO₂) and decreases on further increasing the metal loading just as for HYD and HDS reported earlier.^{5,6} CUS are located on a highly dispersed tungsten phase as a 'patchy monolayer' on the support surface. At higher tungsten loadings a second phase is

formed in addition to the already existing monolayer and this second phase, upon sulphiding, does not chemisorb oxygen significantly at low temperatures. The correlation shown here indicates strongly that the catalytic functionalities of the dispersed tungsten responsible for the HDO are also located on these sites, *i.e.*, on the patchy monolayer phase, and this functionality can be titrated by the LTOC technique.

Table 1 shows the promotional effect of nickel and cobalt on tungsten supported on Al₂O₃ and SiO₂ catalysts. Promoted catalysts were found to be highly active in comparison with unpromoted catalysts. Of the promoted catalysts, the Ni-W system is more active than the Co-W system. It appears that addition of nickel and cobalt increases the HDO activity two to four fold, while the dispersion of W increases only slightly or remains the same. This conclusion is in agreement with the results of Zmierzack *et al.*⁹ and other workers^{3,5-8} on various Mo (W) supported catalysts where the promoted catalysts showed 5-6 times higher activity for HYD and HDS than the unpromoted ones. This agreement suggests that the role of promoter is primarily to increase the intrinsic activity of HDO sites and not to increase their number.

The tungsten loading capacity at the maximum of the 'monolayer' coverage was different for different supports, indicating a specific-catalyst interaction. LTOC measurements can be used as a diagnostic tool for characterizing sulphided W-containing hydroprocessing catalysts. Correlation between LTOC and HDO activity shows that LTOC can be used to measure the active site concentrations on the sulphided form of the catalyst.

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