ELSEVIER

Catalysis Today 29 (1996) 209–213

CATALYSIS TODAY

Hydrodesulfurization of thiophene, dibenzothiophene and gas oil on various Co–Mo/TiO_2–Al_2O_3 catalysts

H. Tanaka [a,*], M. Boulinguiez [b], M. Vrinat [c]

[a] *Japan Energy Corporation, Toda-Shi, Saitama, Japan*
[b] *Elf-Antar France, Solaize, France*
[c] *Institut de Recherches sur la Catalyse, Villeurbanne, France*

Abstract

Evaluation of Co–Mo catalysts prepared on various TiO_2–Al_2O_3 supports has been made for thiophene under atmospheric pressure, dibenzothiophene under high pressure and gasoil in a classical pilot plant. Comparison of activities indicates DBT as more representative of a real feedstock and the Co–Mo/TiO_2 (50%)–Al_2O_3 (50%) catalyst appears more active than the Co–Mo/Al_2O_3 sample toward HDS, HDN and hydrodearomatization.

Keywords: Hydrodesulfurization; Co–Mo/TiO_2–Al_2O_3 catalysts

1. Introduction

The petroleum industry is presently faced with increasingly stringent requirements regarding transportation fuels, in particular diminution of the sulfur content and reduction of the aromatics. For this, development of more active and more selective catalysts has become a challenge for the refiners and many attempts have been made to promote the classical Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 catalysts, or to develop new active phases [1] and new supports [2,3]. Among these new supports, double oxides as TiO_2–Al_2O_3 or TiO_2–ZrO_2 appear to be promising [4].

However, since pilot plant testing with real feedstocks is both time consuming and expensive, there was always interest in devising simple and rapid screening tests for hydrotreating catalysts.

Attempts have been made to correlate activity with H_2, O_2, CO or H_2S uptake of the catalysts [5–9], but none is convincing. Most of the time, activity for hydrodesulfurization was therefore evaluated using thiophene (TH) as a model molecule representative sulfur compounds in commercial feeds and this reaction was invariably performed under atmospheric pressure conditions.

In fact, for deep hydrodesulfurization of gasoil, the polyaromatic sulfur compounds to eliminate have been identified as methyl substituted dibenzothiophene (MDBT) and more precisely 4-MDBT and 4,6-MDBT [10,11]. Moreover, their reactivity is much lower than that of thiophene and use of thiophene in the screening of new catalysts for deep HDS may be misleading.

---

[*] Corresponding author.

SSDI 0920-5861(95)00271-5

In order to address the question of whether the thiophene test gives a reasonable representation of HDS activity of new catalysts, the evaluation and comparison of a series of new catalysts have been undertaken in various reactions. CoMo catalysts prepared over TiO_2–Al_2O_3 supports, have been tested for thiophene under atmospheric pressure, for dibenzothiophene (DBT) at elevated pressure and for gas oil HDS in a pilot plant.

2. Experimental

2.1. Supports preparation

TiO_2–Al_2O_3 mixed oxides covering a full range of composition were prepared by the coprecipitation of aqueous solutions of $TiCl_4$ (acid solution) and $NaAlO_2$ (alkali solution). The hydrogel was separated by filtration, washed with water in a soxhlet, dried at 403 K and finally calcined at 873 K. Detailed of the preparation will been given elsewhere [12].

Recovered solids were grounded, and particles between 80 and 120 μm were used for the preparation of the catalysts. The supports examined in the present study are labelled TiO_2 (x)–Al_2O_3 (y), x and y being the wt.-% of TiO_2 and Al_2O_3, respectively.

For real feedstock experiments, larger amounts of pure Al_2O_3 and TiO_2–Al_2O_3 supports have been prepared as cylindrical shape pellets.

2.2. Catalysts preparation

All the supports were loaded 10 wt.-% Mo and 3 wt.-% Co by successive pore filling impregnation with aqueous solutions of ammonium heptamolybdate and cobalt nitrate, Mo being impregnated first. After each impregnation the catalyst was dried at 393 K overnight and finally calcined at 773 K under an air flow, during 2 h.

Before HDS model reactions, the catalysts were sulfided at atmospheric pressure in a mixture H_2–H_2S (15%) for 2 h at 673 K.

In the case of real feedstock test, the catalyst was sulfided in situ, with a straight run gas oil −2 wt.-% dimethyldisulfide mixture, at 593 K, a total pressure of 35×10^5 Pa and for 12 h.

2.3. Catalytic activities measurements

The catalytic reactions of model compounds were carried out in the vapor phase in dynamic flow microreactors. In order to ensure differential reactor behavior, the catalytic activities have been evaluated at low conversions. The specific rate was determined after 16 h time on stream at the pseudo stationary state according to the following equation:

$$A_s = Q \times \mathrm{TTG}/m$$

where As = specific rate (mol s^{-1} g^{-1}), Q = molar flow-rate of reactant (mol s^{-1}), TTG = conversion and m = weight of catalyst (g).

The HDS of thiophene (TH) was performed at atmospheric pressure with 24×10^2 Pa of

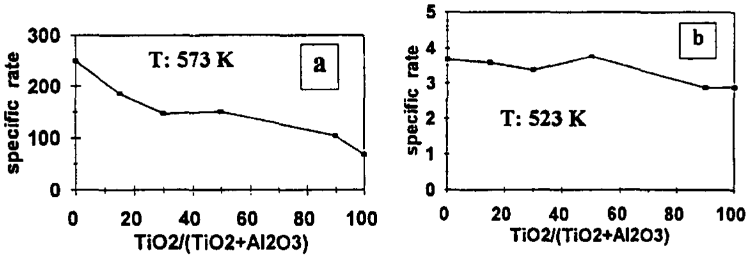

Fig. 1. HDS activities for thiophene (a) and dibenzothiophene (b) in relation with the support composition (rate: 10^{-8} mol s^{-1} g^{-1}).

thiophene, in the reaction temperature range between 553 and 593 K.

The HDS of dibenzothiophene was carried out in a SOTELEM RDP 830 unit, operating at 30×10^5 Pa, with a DBT partial pressure of 520 Pa and H_2S added to the feed flow with a partial pressure of 0.25×10^5 Pa. Experiments were performed between 503 and 543 K.

Heavy gas oil HDS tests were conducted with a conventional fixed bed high pressure flow type unit. Catalyst was diluted with α-alumina balls and experiments performed at 613, 633 and 653 K under pressures of 35×10^5 and 50×10^5 Pa.

3. Results and discussion

3.1. Model compounds HDS reactions

Fig. 1a shows the specific rate for thiophene HDS reaction at 573 K as a function of TiO_2 content in the support. When TiO_2 is added to the support the activity decreases, and for the intermediate composition, where a plateau is observed, the activity is about 40% lower than for pure Al_2O_3 support.

For dibenzothiophene hydrodesulfurization, variation of activity with the support composition is quite different. As indicated in Fig. 1b, the specific activity is more or less constant with increase in TiO_2 content up to 50%, then decreases slowly. These results show that the HDS of thiophene is not correlated with the HDS of dibenzothiophene for CoMo catalysts prepared from different supports.

In the case of DBT, it has been observed that the product distribution markedly changed with TiO_2 content, increasing the TiO_2 content, the formation of cyclohexyl benzene and bicyclohexyl increased at the expense of biphenyl. Moreover, hydrogenated dibenzothiophenes (tetrahydrodibenzothiophene and hexahydrodibenzothiophene) were observed in any case, that amount being stable up to 50% TiO_2 then increased with TiO_2.

As proposed by several workers [13–15], DBT may be desulfurized according to a direct desulfurization (DDS) leading to biphenyl, or by a second reaction pathway in which that molecule is first hydrogenated and then desulfurized, i.e., hydrodesulfurization. Our results about the product distribution suggest that the increase in the TiO_2 content promotes the reaction of DBT desulfurization through the preceding hydrogenation of DBT.

In the case of thiophene, the mechanism proposed by Massoth and Muralidhar [15] does not need hydrogenation of the sulfur molecule before carbon–sulfur bond cleavage. Therefore, differences in reactivity observed between TH and DBT could be related to these different mechanisms and variations in the hydrogenating properties of the catalyst with changes in the support composition would enhance these differences.

Indeed, such variations could also be attributed to differences in operating conditions

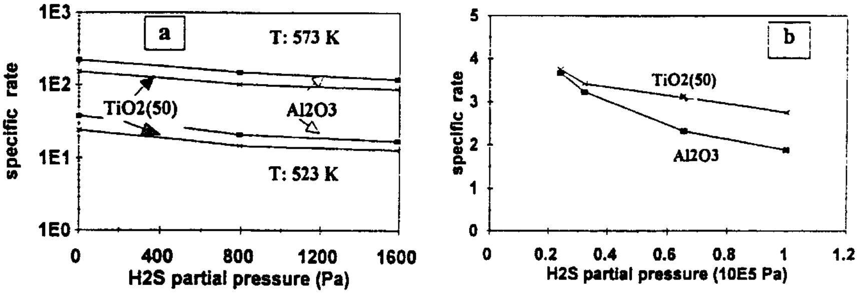

Fig. 2. Effect of H_2S pressure on the HDS of thiophene (a) and dibenzothiophene (b).

since H_2S was added to the feed in the case of DBT.

3.2. Effect of H_2S partial pressure over model compounds HDS

Catalysts prepared over pure Al_2O_3 and TiO_2 (50%)–Al_2O_3 (50%) supports have been studied in thiophene at 523 and 573 K and in DBT at 523 K under a large range of H_2S.partial pressure. Results are given in Fig. 2a and Fig. 2b.

For thiophene, the increase in H_2S partial pressure continuously suppressed the activity in a parallel way for both catalysts.

On the other hand, in the case of DBT, H_2S affected the desulfurization of DBT to different degrees for Co–Mo/Al_2O_3 and Co–Mo/TiO_2(50%)–Al_2O_3(50%) catalysts, the later sample being less sensitive to the inhibiting effect of the additive.

To understand and quantify this different behavior, modelization of H_2S effect was carried out using the following Langmuir–Hinshelwood rate equation proposed in the literature [16] for both HDS of thiophene and dibenzothiophene:

$$r_{\mathrm{HDS}} = k\frac{K_{\mathrm{TH(DBT)}}P_{\mathrm{TH(DBT)}}}{1 + K_{\mathrm{TH(DBT)}}P_{\mathrm{TH(DBT)}} + K_{\mathrm{H_2S}}P_{\mathrm{H_2S}}} \times f(P_{\mathrm{H_2}})$$

k: rate constant; K is equilibrium adsorption constant and P partial pressure, subscripts TH, DBT, H_2S and H_2 refer to thiophene, dibenzothiophene, H_2S and hydrogen, respectively.

Linear relationships between $1/r$ and $P_{\mathrm{H_2S}}$ were obtained and $\frac{K_{\mathrm{H_2S}}}{K_{\mathrm{TH(DBT)}}}$ evaluated. Results given in Table 1 indicate large differences in the inhibiting effect of H_2S. Whatever the organic sulfur molecule considered, inhibition over the TiO_2–Al_2O_3 supported catalyst is lower than over the Al_2O_3 supported sample. That could be related to modifications in the sulfur–support interaction induced by TiO_2, as evidenced by Harle [17] by TPR experiments on Mo/TiO_2–Al_2O_3 catalysts.

Table 1
Relative adsorption constants for H_2S with thiophene or dibenzothiophene

	Al_2O_3	TiO_2 (50%)–Al_2O_3 (50%)
$\frac{K_{\mathrm{H_2S}}}{K_{\mathrm{TH}}}$	1.78	1.23
$\frac{K_{\mathrm{H_2S}}}{K_{\mathrm{DBT}}}$	0.29	0.07

Moreover, compared to thiophene, the DBT adsorption appears less affected by H_2S than thiophene and this difference is particularly evidenced over the Co–Mo/TiO_2 (50%)–Al_2O_3 (50%) catalyst. Such a fact would suggest differences in the adsorption mode of thiophene and dibenzothiophene, i.e., by the sulfur atom for the former and adsorption with the π electron of the aromatic for the latter.

3.3. Gas oil hydrodesulfurization

The gas oil feed (boiling range 517–641 K, density at 288 K: 0.8693) contains 1.43 wt.-% S and 300 ppm N. Experiments have been performed using the same volume of catalyst (50 ml). Example of the relationship between the reaction temperature and the sulfur content in the product oil obtained on each catalyst at the pressure of 50 × 10^5 Pa is shown in Fig. 3.

Estimation of the activation energy indicates that the Co–Mo/TiO_2 (50%)–Al_2O_3 (50%)

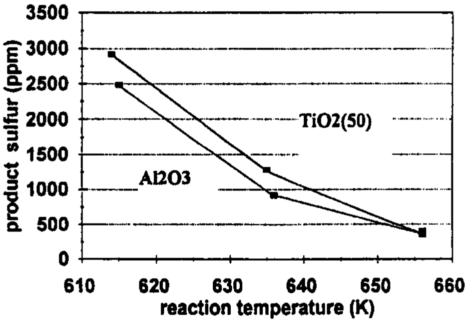

Fig. 3. Sulfur content in the product oil in relation with experimental conditions.

Table 2
Rate constant for gasoil HDS over Al_2O_3 and TiO_2 (50%)–Al_2O_3 (50%) supported catalysts

	613 K, 35 bar	613 K, 50 bar	653 K, 35 bar	653 K, 50 bar
Al_2O_3	0.16	0.17	0.50	0.64
TiO_2–Al_2O_3	0.16	0.17	0.53	0.71

catalyst had about 4 K lower activity than the Al_2O_3 supported sample.

However, comparison could be also made by weight of catalyst and the HDS rate constant was calculated using the following rate equation which relates conversion to residence time:

$$k = \frac{\mathrm{LHSV}}{(n-1)}\left(\frac{1}{S_\mathrm{p}^{n-1}} - \frac{1}{S_\mathrm{f}^{n-1}}\right)$$

where k: rate constant h^{-1}, LHSV: liquid hour space velocity h^{-1}, S_p and S_f: sulfur concentration wt.-% in product and initial feed, and n reaction order taken equal to 1.5. Values of k reported in Table 2 indicate that differences between both catalysts are more pronounced under higher temperatures and pressures. These results indicate that the DBT experiments reflect the real feedstock test, even though the differences of activity observed in the DBT HDS was slightly greater.

Complementary analysis of the nitrogen content and density of the product oil also evidenced variations in the HDN and hydrogenation ability of these two catalysts. Analysis of these results will be published elsewhere [12].

4. Conclusion

Comparison of various Co–Mo/TiO_2–Al_2O_3 catalysts in hydrodesulfurization of thiophene, dibenzothiophene and real feedstock indicates that the low pressure thiophene test does not give accurate results corresponding to catalysts for deep HDS. This could have an important bearing in the search of new catalysts and that appears more significative in the development of molybdenum based catalysts prepared over new supports.

References

[1] M. Breysse, C. Geantet, M. Lacroix, J.L. Portefaix and M. Vrinat, Preprints ACS Div. Petrol. Chem., 39 (1994) 587.
[2] M. Breysse, J.L. Portefaix and M. Vrinat, Catal. Today, 10 (1991) 489.
[3] F. Luck, Bull. Soc. Chim. Belg., 100 (1991) 781.
[4] J. Ramirez, L. Ruiz-Ramirez, L. Cedeno, V. Harle, M. Vrinat and M. Breysse, Appl. Catal. A, 93 (1993) 163.
[5] R. Burch and A. Collins, Appl. Catal., 17 (1985) 273.
[6] J.W. Gosselink and J.H.W. Stork, Bull. Soc. Chim. Belg., 96 (1984) 901.
[7] W.S. Millman, C.H. Bartholomew and R.L. Richardson, J. Catal., 90 (1984) 90.
[8] N.Y. Topsφe, H. Topsφe, O. Sφrensen, B.S. Clausen and R. Candia, Bull. Soc. Chim. Belg., 93 (1984) 727.
[9] J. Bachelier, J.C. Duchet and D. Cornet, J. Catal., 87 (1984) 283.
[10] F. Maruyama, K. Morinaga and T. Suzuka, Proc. First Jpn. EC Joint Workshop Frontiers Catal. Sci. Technol., (1991) 240.
[11] T. Kabe, A. Ishihara and H. Tajima, Ind. Eng. Chem. Res., 31 (1992) 1577.
[12] H. Tanaka et al., in preparation.
[13] M. Houalla, D. H. Broderick, A.V. Sapre, N.K. Nag, V.H.J. de Beer, B.C. Gates and H. Kwart, J. Catal., 61 (1980) 523.
[14] T. Isoda, X. Ma and I. Mochida, Preprint ACS Div. Petrol. Chem., 39 (1994) 584.
[15] F.E. Massoth and G. Muralidhar, Fourth Int. Conf. Chem. Uses Molybdenum, Golden, Colorado, 1982.
[16] M.L. Vrinat, Appl. Catal., 6 (1983) 137.
[17] V. Harle, Thesis Lyon, 1994.