Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc
Petroleum & Coal 51 (2) 146-149, 2009

SUPPORT EFFECT IN HYDRODESULFURIZATION OVER RUTHENIUM SULFIDE

Daniela Gulková, Luděk Kaluža, Zdeněk Vít, Miroslav Zdražil*

Institute of Chemical Process Fundamentals v.v.i., Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Prague 6 - Suchdol, Czech Republic, e-mail: zdrazil@icpf.cas.cz

Received November 27, 2008, accepted April 15, 2009

Abstract

The hydrodesulfurization of thiophene over ruthenium sulfide on Al_2O_3, MgO, SiO_2, TiO_2, ZrO_2 or active carbon was studied. The catalysts (1, 3 and 6 wt.% Ru) were prepared by impregnation with aqueous $RuCl_3$. The only exception was the Ru/MgO catalyst which was prepared by impregnation with methanolic solution of Ru acetylacetonate. The catalysts were sulfided either in a $10\%H_2S/H_2$ or $20\%H_2S/N_2$ mixture at 400 °C. Their activity was tested at 400, 370 and 340 °C. The latter catalysts were mostly more active than the former. The difference increased with the loading and depended on support, the highest being with TiO_2 and ZrO_2 and the lowest with alumina and active carbon. The Ru sulfide catalysts were more active than the Mo/Al_2O_3 catalyst with corresponding loading. The order of activity was independent of activation method and increased in the order $Ru/MgO < Ru/Al_2O_3 \approx Ru/SiO_2 < Ru/ZrO_2 < Ru/TiO_2 < Ru/C$.

Key words: Ruthenium sulfide; Hydrodesulfurization; Support effect; Thiophene.

1. Introduction

Unsupported ruthenium sulfide displayed a prominent hydrodesulfurization activity in comparison with other transition metal sulfides [1]. This was the reason why it has been often studied both in the unsupported and supported form. The literature on alumina-supported Ru sulfide has been summarized in a recent review by De Los Reyes [2]. Ruthenium sulfide has been studied in the unsupported form [3] and on alumina [4-9], carbon [10,11], zeolite [8] and SiO_2 MCM-41 [9]. The impregnation with various Ru salts and various activation methods was studied. A special feature of alumina supported Ru sulfide catalysts is that the activation in a H_2S/N_2 mixture leads to higher activity than conventional activation with a H_2S/H_2 mixture [6,12].

However, no comparison between various supports has been made. The purpose of the present paper was to compare the hydrodesulfurization activity of ruthenium sulfide on Al_2O_3, SiO_2, ZrO_2, TiO_2, C and MgO. The model reaction was hydrodesulfurization of thiophene at increased pressure. The activity of Ru catalysts was compared with a conventional Mo/Al_2O_3 sample.

2. Experimental

2.1. Supports

The origin and surface area of the supports used are summarized in Table 1. All supports were crushed and sieved to the particle size 0.16-0.32 mm. Active carbon was rinsed with water, butanol, dimethyl sulfoxide and water before use. High-surface MgO was prepared from low-surface MgO powder by the hydration-calcination treatment[13].

2.2. Catalysts

Each type of catalyst was prepared with the loading 1, 3 and 6 wt.% Ru. The catalysts with Al_2O_3, ZrO_2, TiO_2, SiO_2 and C support were prepared by impregnation with a water solution of $RuCl_3.3H_2O$. They were dried on a rotary vacuum evaporator and were not calcined. The catalyst $1Ru/Al_2O_3(Cl,un)$ contains 1 % Ru over Al_2O_3, was prepared from ruthenium chloride and was uncalcined. MgO supported catalysts were prepared by impregnation with methanol solution of ruthenium acetylacetonate (MgO support is sensitive to water[14]). They were dried on a rotary vacuum evaporator and were either calcined or uncalcined. Calcination was performed in a fixed-bed flow reactor in an air stream with ramp of temperature 5°C/min to 350°C and dwell 0.5 h at 350°C. 3Ru/MgO(ac,ca) contained 3 % Ru on MgO; it was prepared from acetylacetonate and calcined. The references of activity were the catalysts $1Mo/Al_2O_3$(ahm,ca), $3Mo/Al_2O_3$(ahm,ca) and $6Mo/Al_2O_3$(ahm,ca) prepared by impregnation with water solution of ammonium heptamolybdate and calcined.

Table 1. Supports used

Support	Origin	S_{BET}, m^2g^{-1}
Al_2O_3	AKZO Chemicals HDS-000-1.5, the Netherlands	262
SiO_2	Davisil, grade 646, Sigma Aldrich, product No. 236845, Germany	289
TiO_2	Alfa Aeasar, Product No. 444 29, Germany	140
ZrO_2	Alfa Aesar, Product No. 43815, Germany	108
C	Active carbon GA-05, Hnúšťa, Slovakia	225[a]
MgO	Laboratory made, see text	300

[a] *Surface area in mesopores, with S_{BET} being 1100 m^2g^{-1}.*

2.3. Hydrodesulfurization activity

The model reaction was gas-phase hydrodesulfurization of thiophene (TH) in a fixed-bed flow reactor at a total pressure of 1 MPa. The feed rate of TH, F_{TH}, was 0.909 mmol h^{-1}, and that of hydrogen, F_{H2}, was 0.732 mol h^{-1}. The catalyst charge, W, was 0.035 g; for the most active 6Ru/C catalyst it was 0.01 g. The catalyst was presulfided in situ either with a H_2S/H_2 mixture (1:10) or H_2S/N_2 (1:5) mixture at atmospheric pressure with the temperature program: ramp = 6 °C min^{-1} to 400°C and dwell time = 1 h at 400°C. The TH/H_2 feed was introduced at 400 °C and the pressure 1 MPa. The TH conversion, x_{TH}, was determined at 400, 370 and 340°C. The conversion was defined as $x_{TH} = (n^o_{TH} - n_{TH})/n^o_{TH}$, where n^o_{TH} and n_{TH} are the initial and final number of moles of TH, respectively. The conversion rangede between 0.05 and 0.98, depending on the catalyst and temperature. The test took about 6 h; no deactivation was observed.

It was confirmed with a commercial MoO_3/Al_2O_3 catalyst that the reaction followed the pseudo-first-order rate equation under the conditions used. In these experiments, six catalyst charges were tested and the curve $x_{TH} = f(W/F_{TH})$ well followed the integrated pseudo-first-order-rate equation. The activity of catalyst was evaluated as a pseudo-first-order rate constant k ($mmol_{TH}$ g^{-1} h^{-1}).

3. Results and discussion

For each supported system, three metal loadings at three temperatures were measured and nine rate constants k were obtained. The dependence of k on loading was not linear. An example is shown in Fig. 1. The dispersion of ruthenium sulfide decreased with increased loading.

With the exception of the Ru/MgO catalyst, the compared supported catalysts were prepared by impregnation with water solution of ruthenium chloride, without calcination. For MgO catalysts, a water solution cannot be used because high-surface MgO is not stable in aqueous media – low-surface $Mg(OH)_2$ is formed[14]. That was the reason why the MgO-supported catalysts were prepared by impregnation with a methanolic solution of acetylacetonate. In order to evaluate the effect of calcination, the Ru/MgO(ac,ca) and Ru/MgO(ac,un) catalysts were prepared. For the purpose of comparison we defined the activity index $A(9)$ as the sum of all nine constants at three loadings and three temperatures. The results are shown in Table 2. It can be observed that the differences in activity were small. We have used the data for the Ru/MgO(ac,ca) catalyst in further comparison.

We have also tested the effect of the impregnation compound on activity using the Ru/Al_2O_3(ac,ca), Ru/Al_2O_3(ac,un) and Ru/Al_2O_3(Cl,un) catalysts. The activity indexes *A*(9) after activation in a H_2S/H_2 mixture were 64, 53 and 87, respectively. The catalyst prepared from $RuCl_3$ was thus somewhat better than the catalysts prepared from Ru acetylacetonate. It was concluded that the Ru/MgO(ac)catalyst can be compared, with good approximation, with other catalysts prepared from chlorides.

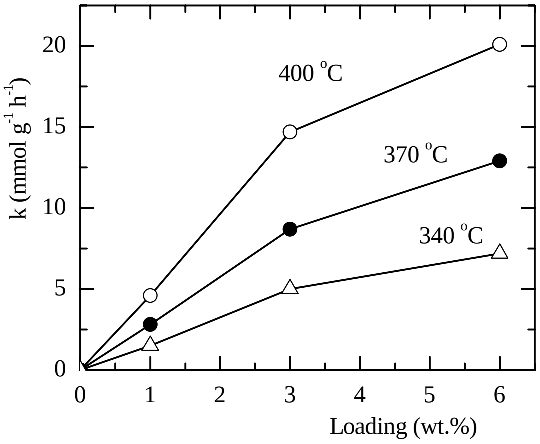

Figure 1. Dependence of rate constant on loading for Ru/SiO_2 catalyst sulfided in H_2S/H_2 mixture.

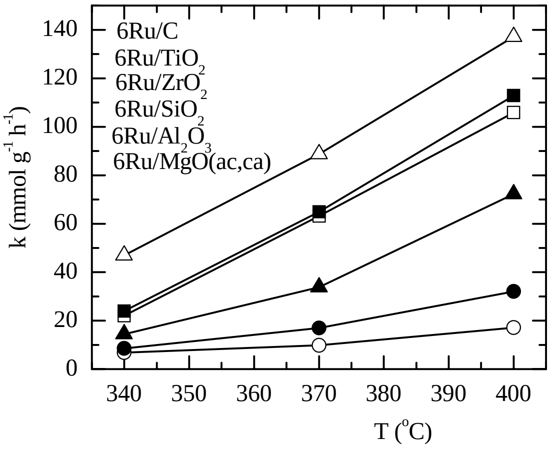

Figure 2. Dependence of rate constant on temperature. The catalysts loading was 6% and they were activated in H_2S/N_2 mixture. The order of catalysts corresponds to order of curves.

Table 2. The effect of calcination on activity index A(9) of Ru/MgO(ac) catalyst

Catalyst	A(9)[a], mmol g^{-1}	
	H_2S/H_2	H_2S/N_2
Ru/MgO(ac,un)	53	49
Ru/MgO(ac,ca)	58	70

[a] *Defined as the sum of all nine constants at three loadings and three temperatures.*

The effect of sulfidation method was compared using the *A*(9) index; the data are shown in Table 3. It is seen that the sulfidation in a H_2S/N_2 mixture provided more active catalysts than the activation in a H_2S/H_2 mixture. The largest difference was observed with the Ru/ZrO_2 catalyst and the lowest for the Ru/Al_2O_3 and Ru/C catalysts. The interesting feature was that the difference increased with catalyst loading. The difference with the catalysts with 1 % loading was low and the difference with 6 % loading was higher. This shows that the formation of sulfide from highly dispersed low-loading catalysts was easier than with poorly dispersed high loading catalysts.

Table 3. Effect of sulfidation method on activity index

Catalyst	A(9)[a], mmol g^{-1} h^{-1}		Ratio
	H_2S/H_2	H_2S/N_2	
Mo/Al_2O_3	70	-	
Ru/MgO(ca)	49	70	1.4
Ru/SiO_2	78	152	1.9
Ru/Al_2O_3	87	106	1.2
Ru/ZrO_2	147	411	2.8
Ru/TiO_2	166	340	2.0
Ru/C	589	765	1.3

[a]*Defined as the sum of all nine constants at three loadings and three temperatures.*

The dependence of the rate constant on temperature for catalysts with 6 % loading is shown in Fig. 2. It can be observed that the difference between the catalysts is higher at higher temperatures. Similar rule was observed with other loadings. That was the reason why the activity of catalysts was compared by means of *k* at 400°C or the activity index *A*(9) including all temperatures.

The comparison by constants *k* at 400 °C is shown in Table 4. It is seen that the ranking of catalysts of various loading is similar. The lowest activity was shown by the Ru/MgO catalyst and the highest activity by the Ru/C catalyst. The difference was rather large, the effect of support was strong. This is also confirmed by the ranking of catalysts by the *A*(9) index in Table 3. The table also shows that the ranking of catalysts was similar for catalysts activated in a H_2S/N_2 and H_2S/H_2 mixture.

Table 4. Activity of catalysts of various loading at 400°C activated in H_2S/N_2 mixture

Catalyst	k, mmol g^{-1} h^{-1}		
	1%	3%	6%
Ru/MgO(ac,ca)	5	7	30
Ru/SiO_2	5	12	30
Ru/Al_2O_3	10	15	32
Ru/ZrO_2	17	60	106
Ru/TiO_2	24	70	113
Ru/C	34	79	137

4. Conclusion

The activity in thiophene hydrodesulfurization of Mo/Al_2O_3, Ru/C, Ru/TiO_2, Ru/ZrO_2, Ru/SiO_2, Ru/Al_2O_3 and Ru/MgO catalysts was tested. The activity of catalysts sulfided in a H_2S/N_2 mixture was higher than that of catalysts sulfided in a H_2S/H_2 mixture. The Ru catalysts were more active than the reference Mo catalyst. The activity strongly depended on the support. The order of decreasing catalyst activity was Ru/C > Ru/TiO_2 > Ru/ZrO_2 > Ru/SiO_2 ≈ Ru/Al_2O_3 > Ru/MgO.

Acknowledgements

Financial support from the Grant agency of the Czech Republic is gratefully acknowledged (grant No. 104/06/0705).

References

[1] Pecoraro, T.A., Chianelli, R.R.: J. Catal. 1981, 67(2), 430
[2] De Los Reyes, J.A: Appl. Catal. A 2007, 322, 106.
[3] Raje, A.E., Liaw, S.J., Srinivasan, R., Davis, B.H.: Appl. Catal. A 1997, 150(2), 297.
[4] Mitchell, P.C.H., Scott, C.E., Bonnelle, J.P., Grimblot, J.G.: J. Catal. 1987, 107(2), 482.
[5] Ishihara, A., Nomura, M., Tabe, K.: J. Catal. 1994, 150(1), 212.
[6] De Los Reyes, J.A., Göbölös, S., Vrinat, M., Breysse, M.: Catal. Lett. 1991, 5(1), 17.
[7] Quartararo, J., Mignard, S., Kasztelan, S.: J. Catal. 2000, 192(2), 307.
[8] Harvey, T.G., Matheson, T.W.: J. Catal. 1986, 101(2), 253.
[9] Eliche-Quasada, D., Rodrígues-Castellón, E., Jiménez-López, A.: Microp. Mesop. Mater. 2007, 99(3), 268.
[10] Hensen, E.J.M., Brans, H.J.A., Lardinois, G.M.H.J, de Beer, V.H.J., Van Veen, J.A.R., van Santen, R.A.: J. Catal. 2000, 192(1), 98.
[11] Ledoux, M., Michaux, O., Agostini, G.: J. Catal. 1986, 102(2), 275.
[12] De Los Reyes, J.A., Vrinat, M., Geantet, C., Breysse, M.: Catal. Today 1991, 10(4), 645.
[13] Gulková, D., Šolcová, O., Zdražil, M.: Microp. Mesop. Mater. 2004, 76(1-3), 137.
[14] Zdražil M.: Catal Today 2003, 86(1-4), 151.