

Novel supported catalyst for hydrodesulfurization reaction

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Thanks to a combination of the high activity of ruthenium and unique properties of a new support, magnesium fluoride, a system highly active in the hydrodesulfurization reaction was obtained.

The petrochemical industry faces a difficult problem of satisfying increasingly restrictive standards for fuels. In particular this problem concerns the reduction of the content of sulfur, nitrogen and aromatic components in the fuels produced, which can be achieved by application of various hydrotreatment processes of crude fuels (HDS, HDN, HDM, HYD and HYC). The sulfided catalysts applied at present, containing molybdenum, cobalt, nickel and tungsten supported on alumina will not be able to comply with future standards of fuel quality. Thus it is necessary to prepare new catalysts for hydrotreatment, which apart from high activity, should be characterized by high HDS selectivity.

In 1981, Pecoraro and Chianelli¹ showed that among transition metal sulfide catalysts, ruthenium systems were the most active. Further studies revealed the dependence of activity of sulfided ruthenium catalysts and the support used. For example Ru supported on alumina^{2,3} was found to have different HDS properties than Ru supported on carbon.⁴

The present results concern thiophene HDS activity at atmospheric pressure. Thiophene was introduced into the reactor by bubbling a stream of pure hydrogen at a rate of 15 cm³ min⁻¹ through a thiophene saturator, maintained in an ice bath at 0 °C. The concentration of thiophene in the feed steam (total flow rate 20 cm³ min⁻¹) was maintained at ca. 2.5 × 10⁻⁴ mol l⁻¹ by adjusting the H₂ flow rate through the saturator. The gas mixtures were analyzed by on-line gas chromatography.

The Ru/MgF₂ catalysts were prepared by conventional impregnation with Ru₃(CO)₁₂, surface area of the support = 40 m² g⁻¹. Magnesium fluoride was obtained from the reaction of MgCO₃ with a 1:1 aqueous solution of HF.⁵ The precipitate was then dried at 110 °C for 24 h and calcined in air at 400 °C for 4 h. The specific properties of magnesium fluoride: hardness, resistance to calcination in oxygen and well developed porous structure enable its application as an active support and owing to the absence of lattice oxygen anions, opens up great possibilities for the study of the structure and texture of the catalyst^{5,6} as well as reaction mechanisms.^{7,8} Additionally the presence of anions of higher electronegativity than oxygen anions leads to the expectation of the appearance of strong interactions between the support and the supported active phase.

The Ru/MgF₂ system containing 1.61% weight of ruthenium was found to be more active than similar samples supported on alumina or silica (Fig. 1). All samples were pretreated in two ways: S, sulfidation in 10% H₂S–H₂ and (ii) OS, calcination in air followed by sulfidation in 10% H₂S–H₂.

As can be seen in Fig. 1, preliminary calcination in air distinctly increases the activity of the samples (apart from those supported on silica). This effect can be explained by much easier sulfidation of calcined samples, which proceeds by the exchange of surface oxygen ions of RuO₂ clusters by sulfur atoms.

Fig. 2 presents the product distribution of thiophene HDS over Ru/MgF₂ and Ru/Al₂O₃. The selectivity of hydrogenation

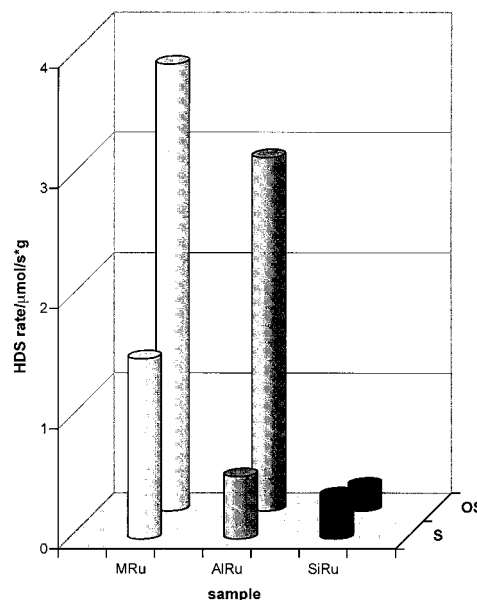


Fig. 1 Comparison of the HDS activity over Ru/MgF₂ (MRu), Ru/Al₂O₃ (AlRu) and Ru/SiO₂ (SiRu) catalysts at 400 °C. S, sulfided in 10% H₂S–H₂, 400 °C, 2 h; OS, calcined in air at 400 °C, 4 h, sulfided in 10% H₂S–H₂, 400 °C, 2 h. The rate of HDS of thiophene is given by HDS rate = FXC/W , where F is the total flow rate of feed, X the fractional conversion, C the concentration of thiophene in the feed and W the catalyst weight.

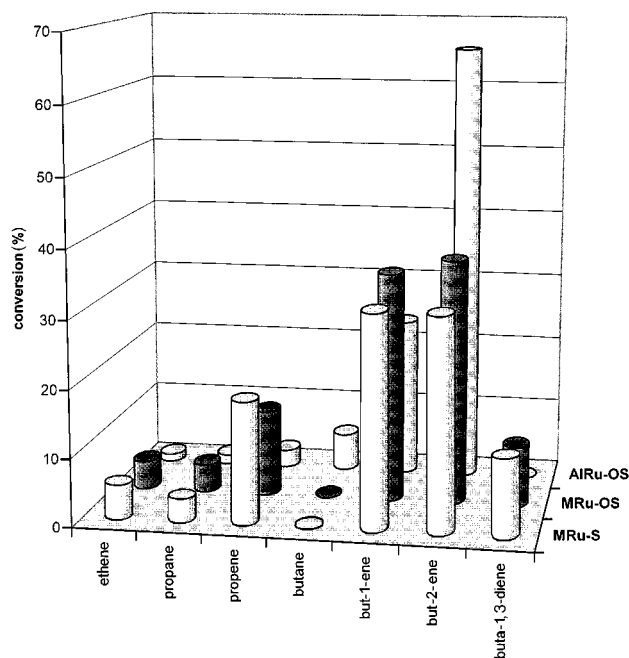


Fig. 2 Product distribution of thiophene HDS over Ru/MgF₂ (MRu) and Ru/Al₂O₃ (AlRu) catalysts. S, sulfided in 10% H₂S–H₂, 400 °C, 2 h; OS, calcined in air at 400 °C, 4 h, sulfided in 10% H₂S–H₂, 400 °C, 2 h.

Table 1 Selectivity of hydrogenation and isomerization

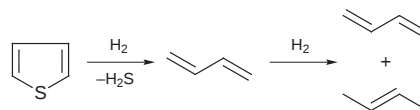
Sample	S_{hyd}	S_{iso}
MRu-S	0.00	1.00
MRu-OS	0.00	0.94
AlRu-OS	0.06	0.36

(S_{hyd}) is defined as the ratio of the formation rates of butane vs. butenes, whereas the ratio of but-1-ene vs. but-2-enes represents the selectivity of isomerization (S_{iso}).

From the above data the conclusion can be made that Ru/MgF₂ catalysts are very selective systems in the HDS process, much less hydrogenation occurs simultaneously with hydrodesulfurization (Table 1) in comparison with Ru/Al₂O₃. This, together with very high HDS activity is a clear advantage of Ru/MgF₂ catalysts compared with other ruthenium systems supported on different supports.

Since the work of Ledoux *et al.*⁹ and Qusro and Massoth,¹⁰ which found a distinct correlation between the HDS activity of thiophene and dibenzothiophene, the results of the HDS reaction for thiophene can be a model example for general conclusions of the hydrodesulfurization activity of the Ru/MgF₂ system.

The lack of tetrahydrothiophene in the reaction products together with the presence of buta-1,3-diene suggests the reaction pathway shown in Scheme 1.¹¹

**Scheme 1**

The catalytic tests for model catalytic reactions of the described samples show a correlation between the thiophene HDS activity and the number of medium strength acidic sites.

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