Hydrodenitrogenation Catalysed by Zeolite-supported Ruthenium

Timothy G. Harvey and Trevor W. Matheson*

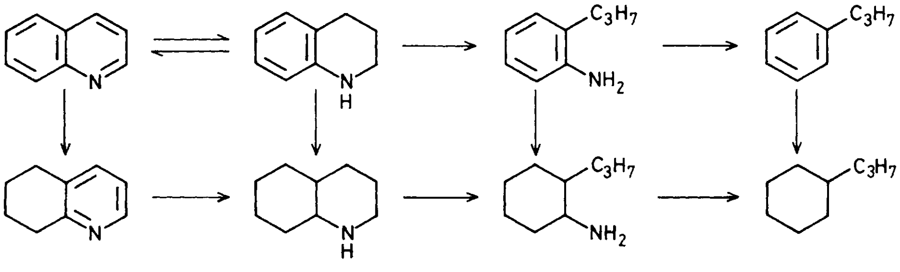
CSIRO Division of Materials Science, Catalysis and Surface Science Laboratory, University of Melbourne, Parkville, 3052 Victoria, Australia

Sulphided ruthenium supported on Y-zeolite is a very active catalyst for hydrodenitrogenation; in combination with sulphided nickel molybdate on alumina the activity is greatly enhanced.

Heavy petroleum residue, shale oil, and coal liquids can contain high levels of organic nitrogen. Nitrogen compounds are poisons for reforming and cracking catalysts, produce NO_x emissions on combustion, and cause poor fuel storage stability; therefore they must be removed or reduced to very low levels.[1] Conventional hydrodenitrogenation catalysts, normally cobalt- or nickel-promoted molybdenum or tungsten sulphides supported on alumina or silica–alumina (~ 15 wt % metal), are not particularly effective at high nitrogen levels[1,2] and new catalysts with higher activity and selectivity are required. This communication deals with a new hydrodenitrogenation catalyst system, based on ruthenium sulphide supported on HY-zeolite, which is highly active at metal loadings (~ 5 wt %) much lower than those used conventionally. The selection of ruthenium was prompted by the high activity of unsupported RuS_2 for the hydrodesulphurization of dibenzothiophene[3] (more active than sulphides of either of the classical hydrotreating metals, molybdenum and tungsten), while the desirable features of zeolites, including high surface area, ability to produce high dispersion of metals, and shape selective capability are applicable to hydrodenitrogenation as they are to other areas of catalysis.[4]

Ruthenium-containing Y-zeolite (3.33% Ru by weight on NH_4Y) was prepared by ion exchange with $[Ru(NH_3)_6]^{3+}$. A reference catalyst, 3.99% Ru by weight on γ-alumina, was prepared by impregnation of alumina (124 $m^2 g^{-1}$) with the same complex. A commercial catalyst [~ 15 wt % MoO_3, ~ 3 wt % NiO supported on alumina (160 $m^2 g^{-1}$)] was used as a second reference; this formulation is considered the best available for hydrodenitrogenation.[1,2] The catalyst systems were air dried (80 °C) then sulphided before use by heating to 350 °C in the presence of sulphur (H_2–H_2S or H_2–CS_2) for 3 h. The ternary metal system was prepared by mechanically mixing sulphided Ni–Mo/Al_2O_3 and RuY (equal weights gave the most active catalyst).

Hydrodenitrogenation experiments were carried out on



Scheme 1. Reaction network for hydrodenitrogenation of quinoline.

Table 1. Catalytic hydrodenitrogenation of quinoline on sulphided catalysts.[a]

	$Ni–Mo/Al_2O_3$ (reference)	RuY	Ru-γ (reference)	$RuY+Ni–Mo/Al_2O_3$ (1 : 1 w/w)
% Conversion	91	91	81	96
% Hydrogenation[b]	44	74	74	44
% Hydrocarbons[c]	5	16	3	26
% n-Propylaniline	43	9	16	22

[a] Conditions: 400 °C, 10 300 kPa; [b] 1,2,3,4-Tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline; decahydroquinoline was not observed; [c] n-Propylcyclohexane, n-propylbenzene.

quinoline as a model nitrogen base, using identical conditions for all catalysts. A small autoclave was charged with catalyst (0.1 g), quinoline (1 g), and n-heptane (15 ml) and cold-filled with hydrogen to 3448 kPa pressure then heated at 400 °C for 4.5 h. Product analysis was by capillary g.c. and g.c.–mass spectroscopy.

The results for all catalysts are shown in Table 1. Hydrogenation is considered to be the first step in hydrodenitrogenation, with cleavage of C–N bonds occurring only in saturated rings (Scheme 1).[1,5] The RuY catalyst, despite its much lower metal loading, compared favourably with the commercial catalyst in overall conversion and C–N bond breaking. A 1 : 1 combination of RuY with a conventional formulation of $Ni–Mo/Al_2O_3$ was even more active for the hydrodenitrogenation of quinoline (Table 1), more so than either of the component catalysts. The synergistic effect, shown by the ternary metal–alumina–zeolite system in the model compound autoclave study, was confirmed using the catalyst for hydroprocessing a shale oil in a continuous reactor. The nitrogen removal and hydrocracking achieved with the new catalyst system for this high-nitrogen, high-boiling feedstock were superior to results for all commercial catalysts tested (including $Ni–Mo/Al_2O_3$, $Co–Mo/Al_2O_3$, and $Ni–W/SiO_2–Al_2O_3$). The ternary metal–alumina–zeolite system shows considerable promise for the direct production of fuels from intransigent feedstock.

The reason for the synergism is unclear. The remote control mechanism for the promotion of hydrodesulphurization catalysts proposed by Delmon[6] may operate in this system. Alternatively, the superior hydrogenation ability of ruthenium (Table 1) may simply increase the availability of 1,2,3,4-tetrahydroquinoline prior to hydrodenitrogenation by ruthenium and molybdenum.

This work was supported by the National Energy Research, Development and Demonstration Programme administered by the Commonwealth Department of National Development.

Received, 26th September 1984; Com. 1368

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