Catalytic Reduction of Dinitroaromatic Compounds with Hydrogen Sulphide–Carbon Monoxide. A Novel, Low-cost Replacement for Elemental Hydrogen

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Summary. A mixed reducing gas consisting of H_2S and CO, when used with sulphided Fe on Al_2O_3 heterogeneous catalysts, has successfully reduced dinitroaromatic to diaminoaromatic compounds in high yield and conversion.

NEW, low-cost reducing agents capable of replacing elemental hydrogen in chemical processes are of increasing interest. Hydrogen sulphide is now a potential major raw material as more high-sulphur crude oil and sour natural gas sources are being utilized. During our study on selective reduction of NO_x to hydroxylamine with H_2S,[1] we discovered the remarkable reducing power which can be achieved when hydrogen sulphide is combined with carbon monoxide and used over sulphided non-noble metal, heterogeneous catalysts. This mixed reducing agent has now been investigated with industrially important nitroaromatic compounds, such as nitrobenzene and dinitrotoluene.

We report the complete conversion of 2,4-dinitrotoluene in $< 0·5$ s contact time at 325 °C to a product containing 2,4-diaminotoluene of high purity with a recovered yield of $> 86\%$ in our laboratory reactor system, reaction (1)]

$$\begin{aligned}&2,4\text{-}(O_2N)_2C_6H_3Me + 6H_2S + 6\,CO \longrightarrow\\&\quad 2,4\text{-}(H_2N)_2C_6H_3Me + 6\,COS + 4\,H_2O\end{aligned} \quad (1)$$

Sulphided group 8 metals on Al_2O_3 are the most effective catalysts for this reaction. The best catalysts for high selectivity have been prepared by standard wet impregnation of 2·5% $Co(NO_3)_2$ on γ-Al_2O_3 (Harshaw 0104) or by wet impregnation of 10% $Fe(NO_3)_3$ on γ-Al_2O_3 (Girdler T-1746) pellets. The catalysts are thermally activated at 500 °C for 1 h followed by treatment with a 20% stream of H_2S at 400 °C for 1 h. A fixed-bed microcatalytic reactor containing 1·36 g of 18/30 mesh catalyst was used for this study. A metered gas stream of 20 cm³ min⁻¹ of N_2, 30 cm³ min⁻¹ of CO, and 30 cm³ min⁻¹ of H_2S was combined with a metered feed of 1·2 g h⁻¹ of a solution containing 20 wt.% of the nitroaromatic compound in toluene. The mixture was passed over a preheated bed of inert quartz chips at 325 °C before contacting the catalyst. The results are in the Table.

TABLE. Gas-phase reduction with H_2S–CO[a]

Reactant	Catalyst	Time/min on stream	*m*-DAB[b]	DAT[c]	MeDAT[d]	———
2,4-Dinitrotoluene	10% Fe_2O_3 on γ-Al_2O_3 (Harshaw 0104 support)	104	9·3	61·0	29·6	
		755		100·0		
		1050		94·8		5·12[e]
,,	5% Co on γ-Al_2O_3 (Harshaw 0104 support)	270	4·5	70·0	25·5	
		715	5·8	81·1	13·1	
2,6-Dinitrotoluene	10% Fe_2O_3 on γ-Al_2O_3 (Girdler T-1746 support)	63	4·5	80·2	15·3[f]	
		454		100·0		
m-Dinitrobenzene	,,	45	100·0			
		238	71·9			20·9[g]

[a] Conditions for all reactions: 325 °C, 0·4 s contact time, fixed bed microflow reactor, 100% conversion in all cases. [b] *m*-Diaminobenzene. [c] 2,4- or 2,6-Diaminotoluene. [d] 4,6-Diamino-*m*-xylene. [e] 4-Amino-2-nitrotoluene. [f] Diaminoxylene, isomeric structure not yet identified. [g] *m*-Aminonitrobenzene.

A potential secondary reaction of urea formation *via* the reaction of amine products with CO was not observed under our short residence-time flow conditions. Intermolecular alkylation of diaminotoluene to form *m*-diaminobenzene with methyl addition to diaminotoluene was the major side reaction, the extent of which decreased after 5 h on stream with iron sulphide-impregnated γ-Al_2O_3 catalysts.

The mechanism for H_2S–CO reduction on our sulphided catalysts involves strong chemisorption of H_2S on the surface, as also observed in earlier studies by Owens and Amberg[2] on supported catalysts. In the absence of CO, electron transfer from chemisorbed H_2S to adsorbed nitro-groups initially occurs with the oxidation of sulphide to form free sulphur as an observed product. A rapid decline in activity in the absence of CO was accompanied by a phase change in the cobalt component, with the active Co_3S_4 phase being degraded to an apparently inactive CoS_2 phase. The Co_9S_8 phase associated with Co–Mo hydrosulphurization catalysts[3] was not observed under these conditions involving high concentrations of H_2S or H_2S–CO. The presence of CO in the reactant stream, however, allowed the catalyst to maintain high activity with the removal of sulphur as carbonyl sulphide. The role of CO in the reduction process can be viewed as the gas-shift reaction (2). The formation of 'nascent' hydrogen atoms

$$H_2S + CO \rightleftharpoons COS + H_2 \qquad (2)$$

on the catalyst surface would result in a rapid reaction with adsorbed nitroaromatic compounds. Metal sulphides are known to catalyse this reaction, as recently reported by Fukuda, *et al.*[4]

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