

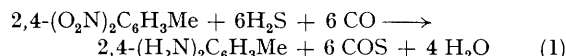
## Catalytic Reduction of Dinitroaromatic Compounds with Hydrogen Sulphide–Carbon Monoxide. A Novel, Low-cost Replacement for Elemental Hydrogen

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**Summary** A mixed reducing gas consisting of H<sub>2</sub>S and CO, when used with sulphided Fe on Al<sub>2</sub>O<sub>3</sub> heterogeneous catalysts, has successfully reduced dinitroaromatic to diaminoaromatic compounds in high yield and conversion

2,4-diaminotoluene of high purity with a recovered yield of > 86% in our laboratory reactor system, reaction (I)]



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<sub>x</sub> to hydroxylamine with H<sub>2</sub>S,<sup>1</sup> 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

Sulphided group 8 metals on Al<sub>2</sub>O<sub>3</sub> 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<sub>3</sub>)<sub>2</sub> on γ-Al<sub>2</sub>O<sub>3</sub> (Harshaw 0104) or by wet impregnation of 10% Fe(NO<sub>3</sub>)<sub>3</sub> on γ-Al<sub>2</sub>O<sub>3</sub> (Girdler T-1746) pellets. The catalysts are thermally activated at 500 °C for 1 h followed by treatment with a 20% stream of H<sub>2</sub>S 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 cm<sup>3</sup> min<sup>-1</sup> of N<sub>2</sub>, 30 cm<sup>3</sup> min<sup>-1</sup> of CO, and 30 cm<sup>3</sup> min<sup>-1</sup> of H<sub>2</sub>S was combined with a metered feed of 1.2 g h<sup>-1</sup> 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<sub>2</sub>S–CO<sup>a</sup>

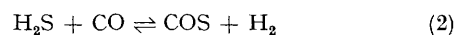
Reactant	Catalyst	Time/min on stream	<i>m</i> -DAB <sup>b</sup>	DAT <sup>c</sup>	MeDAT <sup>d</sup>	————
2,4-Dinitrotoluene	10% Fe <sub>2</sub> O <sub>3</sub> on γ-Al <sub>2</sub> O <sub>3</sub> (Harshaw 0104 support)	104	9.3	61.0	29.6	
		755		100.0		
		1050		94.8		5.12 <sup>e</sup>
,,	5% Co on γ-Al <sub>2</sub> O <sub>3</sub> (Harshaw 0104 support)	270	4.5	70.0	25.5	
		715	5.8	81.1	13.1	
2,6-Dinitrotoluene	10% Fe <sub>2</sub> O <sub>3</sub> on γ-Al <sub>2</sub> O <sub>3</sub> (Girdler T-1746 support)	63	4.5	80.2	15.3 <sup>f</sup>	
		454		100.0		
<i>m</i> -Dinitrobenzene	,,	45	100.0			
		238	71.9			20.9 <sup>g</sup>

<sup>a</sup> Conditions for all reactions: 325 °C, 0.4 s contact time, fixed bed microflow reactor, 100% conversion in all cases. <sup>b</sup> *m*-Diaminobenzene. <sup>c</sup> 2,4- or 2,6-Diaminotoluene. <sup>d</sup> 4,6-Diamino-*m*-xylene. <sup>e</sup> 4-Amino-2-nitrotoluene. <sup>f</sup> Diaminoxylene, isomeric structure not yet identified. <sup>g</sup> *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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

The mechanism for H<sub>2</sub>S-CO reduction on our sulphided catalysts involves strong chemisorption of H<sub>2</sub>S on the surface, as also observed in earlier studies by Owens and Amberg<sup>2</sup> on supported catalysts. In the absence of CO, electron transfer from chemisorbed H<sub>2</sub>S 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<sub>3</sub>S<sub>4</sub> phase being degraded to an apparently inactive CoS<sub>2</sub>

phase. The Co<sub>9</sub>S<sub>8</sub> phase associated with Co-Mo hydro-sulphurization catalysts<sup>3</sup> was not observed under these conditions involving high concentrations of H<sub>2</sub>S or H<sub>2</sub>S-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



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.*<sup>4</sup>

(Received, 14th September 1979; Com. 991.)

<sup>1</sup> C. T. Ratcliffe, U.S. P. 4,115,523.

<sup>2</sup> P. J. Owens and C. H. Amberg, 'Solid Surfaces and the Gas Solid Interphase,' Advances in Chemistry Series No. 33, ed. R. F. Gould, American Chemical Society, 1961, pp. 182-198.

<sup>3</sup> P. Grange and B. Delmon, *J. Less-Common Met.*, 1974, **36**, 353.

<sup>4</sup> K. Fukuda, M. Dokiya, T. Kameyama, and Y. Kotera, *J. Catal.*, 1977, **49**, 379.