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SELECTIVE REDUCTION OF NITROBENZENE TO NITROSOBENZENE ON OXIDIC CATALYSTS

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Pure unpromoted Mn_3O_4 appears to be a very suitable catalyst for the selective reduction of nitrobenzene to nitrosobenzene; the oxygen vacancies required to split off oxygen atoms can be created both by the phenyl group of nitrobenzene itself and by an additional reducing agent like e.g. methane.

In heterogeneous catalysis, a large number of selective oxidation reactions has been extensively studied already [1–3]. In the case of oxide catalysts the mechanism of reactions is well established. It can be described by the so-called "redox" principle as postulated by Mars and van Krevelen [4]. In this mechanism a reducing reactant is selectively oxidized by lattice oxygen of the catalyst to a (valuable) product, creating oxygen vacancies in the catalyst. The reoxidation of the catalyst, i.e. the replenishment of these oxygen vacancies, is mostly performed by molecular oxygen.

So far, very little attention has been paid to the possibility of using the reoxidation step to obtain desirable products from the oxidizing agent. Therefore, the selective reduction of nitrobenzene to nitrosobenzene has been chosen as a model reaction in this investigation. This one-step reduction of nitro compounds is moreover a commercially interesting reaction, for the corresponding nitroso analogues are quite useful because of their high reactivity in a large variety of reactions [5].

Dodman et al. found that modified manganese oxides are very suitable for this reaction [6]. However, it has not been known up to now whether the modified MnO_x catalysts are unique for this purpose. Also it has not been established yet so far that the modification of MnO_x is a necessary prerequisite in obtaining selective catalysts. Therefore, the catalytic performance of pure manganese oxide has been determined here and is compared with that of two "classical" redox catalysts, namely vanadium oxide and molybdenum oxide.

V_2O_5 and MoO_3 were obtained by thermal decomposition of NH_4VO_3 (700 K, 24 h) and $(NH_4)_6Mo_7O_{24}$ (900 K, 40 h) respectively. Mn_3O_4 was prepared from

$Mn(OH)_2$ by mild calcination in air (400 K, 24 h). The catalytic measurements were performed in a continuous flow system with a fixed bed reactor using helium as a carrier gas and methane as a reducing agent (523 K and 573 K, total pressure 101 kPa, nitrobenzene partial pressure 1.2 kPa). Reaction was followed by GC analysis of the reaction mixture.

The activity of the catalysts is characterized by the percentage of nitrobenzene totally converted, α. The percentage of nitrobenzene converted to nitrosobenzene is called the yield of nitrosobenzene (y_{PhNO}). Conversions are kept low throughout all experiments (differential reactor) to avoid complications by extended consecutive reactions. Selectivities are characterized by the percentage of a certain product related to the amount of nitrobenzene reacted. These are almost independent of α in the region of α measured. "$PhNO_2$ oxidized" has been defined as the amount of nitrobenzene fully oxidized to CO_2, CO, etc. Because it is not possible to discriminate between CO and CO_2 originated from CH_4 and that originated from nitrobenzene, the amount of "$PhNO_2$ oxidized" has been determined from the mass balance of the amount of nitrobenzene in the feed and the sum of all compounds detected by flame ionization. Other by-products were aniline and small quantities of benzene and dimerized products like azobenzene and azoxybenzene.

Experiments show that when the starting state of the catalyst is pure manganese dioxide, very high selectivities to nitrosobenzene (80–90%) can be obtained. However, this occurs only after an induction period lasting more than 24 hours. This induction period can be shortened by applying a mild prereduction of the catalyst. X-ray diffraction and IR measurements show that during the prereduction or during the induction period, the catalyst is completely reduced to α-Mn_3O_4 (Hausmannite), which is the active phase for the selective reduction of nitrobenzene.

A comparison of oxides is in table 1. The table indicates whether an external reducing agent (CH_4) was (+) or was not (−) present in the reaction mixture.

Table 1 shows that all three catalysts are able to convert nitrobenzene very selectively into nitrosobenzene when an external reducing agent like methane is used. It can be concluded from the nitrosobenzene yields per unit fo surface area (last column of table 1) that Mn_3O_4 is a better catalyst in the selective reduction of nitrobenzene to nitrosobenzene than both V_2O_5 and MoO_3.

However, on using all three catalysts the nitrosobenzene yield is hardly affected by performing the reaction in absence of methane. The role of methane as a reducing agent appears to be taken over by the phenyl group of nitrobenzene, resulting in a higher over-all conversion of nitrobenzene and a relatively poor selectivity to nitrosobenzene. The function of nitrobenzene as the internal reducing agent has been already suggested by Zengel et al., who assumed an autoredox mechanism for the selective reduction to nitrosobenzene in absence of other reducing agents [7].

Table 1
Results of the catalytic measurements at standard conditions (PhNO stands for nitrosobenzene; $PhNH_2$-aniline; $PhNO_2$-nitrobenzene)

catalysts	W (g)	S_{BET} (m^2/g)	T (K)	CH_4	α (%)	selectivities (%)				y_{PhNO}	
						PhNO	PhNH2	PhNO2 ox. to CO_x	other compounds	(%)	*
Mn_3O_4	0.30	30.2	573	+	14.3	90	10	0	0	12.9	1.23
Mn_3O_4	0.15	28.1	573	–	15.1	38	3	57	2	5.74	1.18
Mn_3O_4	0.30	50.0	523	+	9.0	85	8	0	7	7.65	0.44
V_2O_5	0.40	11.6	573	+	1.88	96	2	0	2	1.80	0.34
V_2O_5	0.30	9.9	573	–	5.35	32	0	67	1	1.71	0.50
MoO_3	1.50	2.0	573	+	1.08	98	0	0	2	1.06	0.31
MoO_3	1.50	2.4	573	–	1.71	54	0	45	1	0.92	0.22

* In 10^{15} molecules·sec^{-1}·m^{-2}.

There has been done no further research on the exact reason why the presence of CH_4 suppresses the oxidation of the phenyl ring. However, it is likely that this can be related to the fact that the C-H bond dissociation energy is about 26 kJ/mol lower for methane than for benzene [8,9].

Summarizing the following conclusions can be presented:

(i) The reoxidation step of oxide catalysts can be used for the selective reduction of nitrobenzene.

(ii) Unpromoted pure manganese oxide is -contrary to the statements in the patent literature- a good catalyst for this reaction. The nitrosobenzene yield per unit of surface area of Mn_3O_4 is about three to five times higher than that of V_2O_5 and MoO_3.

(iii) The active phase appears to be α-Mn_3O_4.

(iv) An autoredox reaction is observed in absence of methane, demonstrating the dual behaviour (both reducing and oxidizing) of nitrobenzene.

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