

Copper exchanged beta zeolites for the catalytic oxidation of ammonia

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Copper exchanged on beta zeolites are extremely active and selective for the catalytic oxidation of ammonia to nitrogen and water and this activity correlates to the ease of reduction of the copper species.

Ammonia is a well-known gaseous pollutant that has several adverse effects on the atmosphere. For example, ammonia emissions contribute to the acidification of the environment and its precursors are responsible for the greenhouse effect and city smog. Many techniques are available for the abatement of ammonia such as adsorption, biological purification and catalytic decomposition. Each has its disadvantages, for example, in catalytic decomposition, ammonia decomposes in the absence of oxygen into nitrogen and hydrogen using a platinum–ceramic membrane catalyst.¹ However, temperatures of over 600 °C are required for this process. An alternative method for ammonia destruction is the catalytic oxidation of ammonia to nitrogen and water, which operates at lower temperatures.

The earliest reported work on the catalytic oxidation of ammonia concerned a detailed study over unsupported metal oxides at temperatures between 160–370 °C.² The products of reaction observed were nitrogen, water and NO. Activity could be improved by supporting the metal oxide and several publications now exist showing that ammonia can be converted to nitrogen and water in the presence of oxygen over metal oxide supported catalysts. Examples include MoO₃/SiO₂,³ V₂O₅/TiO₂ and CuO/TiO₂,⁴ NiO/Al₂O₃,⁵ CuO/Al₂O₃,^{6,7} and Fe₂O₃/TiO₂.⁸ For most of these publications by-products N₂O and NO are also formed in varying amounts.

One of the first reports on the catalytic oxidation of ammonia using exchanged zeolites was recorded by Golodets over a series of cation exchanged Y zeolites.⁹ Copper exchanged ZSM-5 was also reported as a potential catalyst for the oxidation of ammonia and showed promising results.^{4,10} More recently, both Cu and Fe exchanged on ZSM5 showed high activity for oxidation of ammonia with low levels of NO and N₂O produced.¹¹

A feature of most catalysts presented to date is the dramatic fall in activity when water vapour is introduced into the stream. In general, this effect does not adversely affect the selectivity to nitrogen.^{12,13} This work presents ammonia oxidation over a series of copper exchanged beta zeolites. These catalysts have not been reported before for the catalytic oxidation of ammonia. The effect of water is also presented.

Copper exchanged beta zeolites (Si/Al = 25, Zeolyst International) were prepared using a procedure outlined by Iwamoto *et al.*¹⁴ The copper oxide impregnated on alumina (Rhône-Poulenc, 134 m² g⁻¹) catalyst was prepared by conventional dry impregnation using copper nitrate. All prepared catalysts were dried and then calcined at 450 °C for 5 hours in air. Following calcination, the catalysts were sieved to a particle size 106–225 µm. The copper content of the prepared catalysts was determined using atomic absorption (A.A.). The catalyst nomenclature used throughout the paper includes the copper content, the support and the method of preparation. For example, 6.6Cu/beta(ex) indicates a catalyst containing 6.6 wt.% copper (measured by A.A.) on beta zeolite prepared by ion

exchange. Temperature Programmed Reduction (TPR) using 5% H₂ in N₂ (heating rate 10 °C min⁻¹) was performed on all catalysts and on some catalysts following exposure to water.

Ammonia oxidation testing was carried out in a continuous flow system operated at ambient pressure. All catalysts (25 mg) were pre-treated at 420 °C for 90 minutes in a flow of 20 ml min⁻¹ helium before testing. The reactor was a quartz glass vertical tube and the catalyst was kept in position by two plugs of quartz wool. The temperature of the catalyst was monitored by a thermocouple, which was outside the reactor close to the catalyst bed. Typically, the gas composition used was 0.54% NH₃, 8% O₂ with a balance of helium. The gases leaving the catalytic reactor were analysed using a Hewlett-Packard HP5971A Mass Selective Detector. In some experiments, 1% H₂O was added to the reactant stream *via* a water saturator. All data were recorded between 5 and 12 hours on stream.

Fig. 1 presents ammonia conversion with temperature for the prepared copper exchanged zeolites. For comparison a 4.3 wt.% copper oxide on alumina catalyst is also presented as this was shown to be one of the most active catalysts tested to date.⁷ Ammonia conversion increased with temperature for all catalysts and ammonia conversion also increased with copper content for the copper exchanged beta catalysts. Indeed, the 6.6Cu/beta catalyst proved to be extremely active, presenting almost complete conversion even at temperatures as low as 250 °C. A promising feature of these catalysts was the very high selectivity to nitrogen with little or no NO detected (see Table 1). Low levels of N₂O were observed, however in comparison to 4.3CuO/Al₂O₃, a marked improvement was observed in terms of minimising formation of by-products. This high selectivity to nitrogen and high activity makes the copper exchanged beta catalyst one of the most active catalysts reported to date in the literature for the oxidation of ammonia to nitrogen in the presence of oxygen.

Introducing water vapour (1 vol%) into the reactant stream resulted in a fall in activity for all catalysts. For example, ammonia conversion fell to 5% from 25% with the introduction of water for the 1.2Cu/beta catalyst. This represented a loss in activity of 80%. However, this loss in activity was less severe

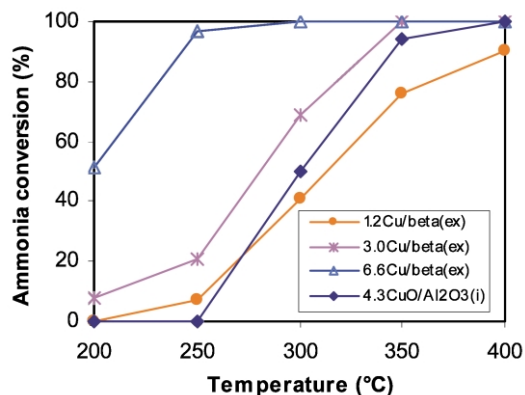


Fig. 1 Ammonia conversion, with temperature, using the indicated copper catalysts. Reaction conditions: 0.54% NH₃, 8% O₂, balance He; 25 mg catalyst; W/F 0.015 g s ml⁻¹.

Table 1 Selectivity to various products with temperature for the indicated catalysts^a

Temp./°C	1.2Cu/beta			3.0Cu/beta			6.6Cu/beta			4.3CuO/Al ₂ O ₃		
	N ₂	NO	N ₂ O	N ₂	NO	N ₂ O	N ₂	NO	N ₂ O	N ₂	NO	N ₂ O
200	—	—	—	97	2	1	97	0	3	—	—	—
250	95	1	4	95	2	3	96	0	4	—	—	—
300	97	1	2	96	2	2	96	0	4	93	3	4
350	98	1	1	96	2	2	96	0	4	75	10	15
400	98	1	1	98	1	1	98	0	2	51	23	26

^a Reaction conditions: 0.54% NH₃, 8% O₂, He balance; 25 mg catalyst; W/F 0.015 g s ml⁻¹.

when the copper content of the beta zeolite was higher. This is shown in Fig. 2. The 4.3CuO/Al₂O₃ catalyst is included for comparison (*i.e.* 3.4 wt.% Cu). The 6.6Cu/beta catalyst presented a fall in conversion of less than 30%, indicating that the copper content of the beta zeolite is not only important for the activity but is also important for operation in the presence of water vapour. It seems that the copper species present at higher loadings is less affected by the action of water vapour. This is an important aspect that is currently undergoing further investigation. Selectivity was not affected by the introduction of water.

The copper exchanged beta catalysts were subjected to temperature programmed reduction. These catalysts exhibited hydrogen consumption peaks, which correspond to a mixture of Cu²⁺ species and CuO aggregates on the beta zeolite. The level of hydrogen consumed increased with copper content for these catalysts and the temperature required for reduction decreased. In fact there is a linear relationship between the copper reduction temperature and ammonia conversion. This is seen graphically in Fig. 3 (closed symbols) at 325 °C with a W/F of 0.0075 g s ml⁻¹. The most active catalyst exhibited the lowest copper reduction temperature. Therefore, it seems that the reducibility of the copper species in the zeolite is important in promoting an active ammonia oxidation catalyst. In comparison to copper exchanged ZSM-5 zeolites reported in the literature, beta exchanged zeolites are more active.^{4,10,11} This may be due in part to the larger pore opening of the beta in comparison to ZSM-5 which may enhance diffusion of the reactants and promote the formation of CuO aggregates which are easily reduced. These aggregates seem to have an important role in promoting activity.

The 3.0Cu/beta and 6.6Cu/beta catalysts were tested in wet conditions (0.54% NH₃, 1.0% H₂O, 8% O₂, balance He; 25 mg catalyst; W/F 0.0075 g s ml⁻¹; 325 °C) for several hours and subsequently the used catalysts were subjected to TPR analysis following the standard procedure. For both catalysts the reduction temperature was higher compared to the corresponding fresh catalyst. These two catalysts (open symbols) are included in Fig. 3 and it can be seen that the reduction

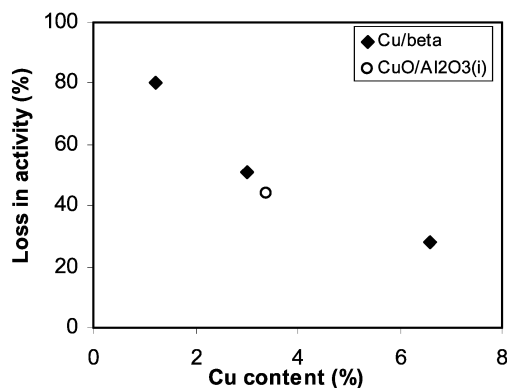


Fig. 2 Loss in activity with the introduction of water versus catalyst copper content. Reaction conditions: 0.54% NH₃, 1.0% H₂O, 8% O₂, balance He; 25 mg catalyst; W/F 0.0075 g s ml⁻¹; 325 °C.

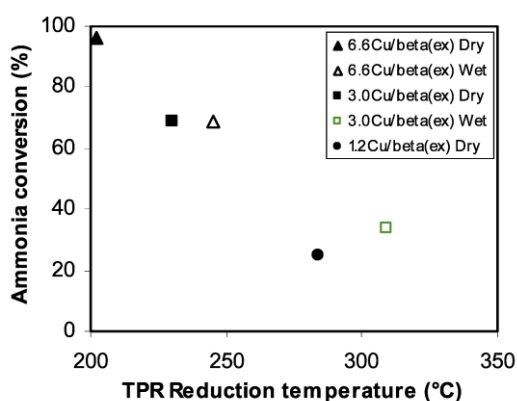


Fig. 3 Ammonia conversion with TPR reduction temperature of the indicated catalysts. Reaction conditions: 0.54% NH₃, (1.0% H₂O), 8% O₂, balance He; 25 mg catalyst; W/F 0.0075 g s ml⁻¹; 325 °C.

temperature corresponds well with ammonia conversion. Therefore, it seems that the water alters the copper species in the zeolite, which in turn leads to a fall in conversion. The effect is greatest for the lower copper containing zeolite.

In conclusion, copper exchanged beta zeolites proved to be extremely active for the catalytic oxidation of ammonia to nitrogen and water. The most promising feature is the low level of NO and N₂O formed. Water vapour does not affect selectivity to nitrogen although it does have an adverse effect on overall activity. Increasing the copper content can reduce this negative influence.

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