

A novel basic alkaline-earth zeolite-supported ruthenium catalyst for ammonia synthesis

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Ruthenium clusters supported on basic zeolites containing alkaline-earth cations catalyse ammonia synthesis with reaction rates that exceed those for analogous catalysts containing only alkali-metal cations.

Ruthenium metal supported on activated carbon and promoted by alkali metals is emerging as a second-generation ammonia synthesis catalyst,¹ succeeding the conventional iron-based technology. However, activated carbon is not considered an ideal support material since Ru catalyses both oxidation² and methanation³ of carbon. One family of alternative supports, alkali-metal zeolites X and Y, was recently studied by Mahdi *et al.*⁴ and Cisneros and Lunsford.⁵ The turnover frequencies, based on surface metal atoms, for ammonia synthesis over Ru/zeolites were lower than that reported for Ru on activated carbon, but the percentage of Ru exposed was higher using zeolite supports.⁵ Thus, on the basis of catalytic activity per total number of Ru atoms, the Ru/zeolite systems compared more favourably. However, improvements in the activity of Ru/zeolite catalysts are still necessary before they can be viable replacements for carbon-supported materials.

The approach used by Cisneros and Lunsford to improve the activity of Ru/zeolites was to adjust the partial oxygen charge of a zeolite X support by incorporating alkali-metal cations (Na, K, Cs).⁵ They observed that as the partial charge of the zeolitic oxygen became more negative, the turnover frequency for ammonia synthesis increased. In this communication, we report a remarkable promotional effect of alkaline-earth cations on the catalytic activity of Ru/zeolites that exceed that of alkali-metal cations.

The starting material for the ammonia synthesis catalysts was NaX. Zeolite KX was prepared by ion-exchange of NaX with 1 mol dm⁻³ KNO₃ at room temperature, followed by filtering and drying. A catalyst with a nominal metal loading of 2 mass% Ru was then made by ion-exchange of KX with [Ru(NH₃)₆]Cl₃. After exchange, this Ru/KX was filtered and washed with distilled deionized water to remove chloride ions. The Ru/KX was then reduced in flowing dihydrogen at 723 K before any further ion-exchanges were performed. Portions of the reduced Ru/KX were ion-exchanged at room temperature with 1 mol dm⁻³ caesium acetate, calcium acetate, or barium acetate. Any acidic sites introduced during these exchanges were neutralized by impregnation with 0.2 molal aqueous solutions of the appropriate alkali metal or alkaline-earth hydroxides. For alkali-metal containing materials, the final impregnation increased catalytic activity by *ca.* 20–30%.

Ruthenium supported on MgO was prepared by impregnation of a high surface-area MgO provided by Ube Industries⁶ with [Ru₃(CO)₁₂] dissolved in THF. After impregnation, the Ru/MgO was air dried overnight at room temperature. This material was then heated *in vacuo* at 0.5 K min⁻¹ to 723 K to decompose the carbonyl. The ruthenium was reduced in H₂ at 723 K for 2 h and then cooled to room temperature. Since previous studies with zeolite supports have shown that the Ru metal precursor does not influence the catalytic activity of the final catalyst,⁵ a comparison of a zeolite catalyst prepared with [Ru(NH₃)₆]Cl₃ to a magnesia catalyst synthesized with Ru₃(CO)₁₂ is valid.

The ammonia synthesis reaction was studied over the temperature range 590–740 K using an atmospheric pressure, closed-loop recirculation system. All samples were dehydrated and reduced *in situ* in the same manner as described above before catalytic testing. The system was evacuated to <10⁻⁵ mbar and a mixture of H₂ and N₂ in a 3:1 molar ratio was admitted at atmospheric pressure. As the reactants passed over the catalyst and circulated through the system, the ammonia produced was condensed in a liquid-nitrogen trap to prevent the reverse NH₃ decomposition reaction from occurring. The forward reaction rate was monitored by measuring the linear pressure drop over time with a high-accuracy pressure gauge (MKS Baratron).

The results from elemental analysis of the catalyst samples (Galbraith Laboratories, Knoxville, TN, USA) and static dihydrogen chemisorption are given in Table 1. Unit-cell compositions of the zeolites are based on the assumption of 384 oxygen connected to Si and Al tetrahedra with a Si/Al molar ratio matching that determined from elemental analysis. Protons were added to unit-cell formulae to balance the framework charge, when necessary. Ion exchange of K for Na is nearly complete in our KX sample whereas Cs exchange for K results in a lower level of incorporation.⁷ Hydrogen chemisorption indicates that a large fraction of the Ru in the metal clusters is exposed to the surface. The H/Ru ratios presented in Table 1 are consistent with metal cluster sizes ranging from 1 to 1.3 nm in diameter, assuming spherical cluster geometry. Since the internal diameters of the zeolite X sodalite cage and supercage are 0.7 and 1.3 nm, respectively,⁷ the clusters are most likely located inside the supercages. For comparison, we synthesized ruthenium clusters of about the same size supported on MgO.

Turnover frequencies and activation and energies for the reaction are listed in Table 2. Each of the catalysts exhibited an activation energy of *ca.* 100 kJ mol⁻¹ which compares favourably with numerous studies on supported Ru catalysts.^{5,8,9} The observation that Ru/CsX is more than twice as active as Ru/KX differs from earlier work with ruthenium zeolites⁵ probably because we were able to incorporate a much greater amount of Cs into the zeolite. Our work verifies that ruthenium clusters supported on zeolite X can be promoted with alkali-metal cations in a similar way to ruthenium clusters on

Table 1 Description of catalysts used for ammonia synthesis

Catalyst	Ruthenium loading /mass%	H/Ru ^a	Support composition
Ru/KX	2.04	0.93	K _{66.7} Na _{4.1} H _{7.5} Si _{113.7} Al _{78.3} O ₃₈₄
Ru/CsX	2.01	0.72	Cs _{84.9} K _{15.5} Na _{9.8} H _{1.6} Si _{120.2} Al _{71.8} O ₈₃₄
Ru/CaX	2.21	0.83	Ca _{55.2} K _{12.7} Si _{116.0} Al _{76.0} O ₃₈₄
Ru/BaX	2.05	0.92	Ba _{41.8} K _{10.5} Si _{109.6} Al _{82.4} O ₃₈₄
Ru/BaX(2)	2.10	0.79	Ba _{35.6} K _{8.5} Si _{116.1} Al _{75.9} O ₃₈₄
Ru/MgO	2.52	0.87	MgO

^a Ratio of chemisorbed H atoms to total Ru atoms in sample obtained by extrapolation of the linear part of dihydrogen adsorption isotherm (5–30 kPa) to zero pressure.

non-zeolite supports. For example, for ruthenium clusters supported on carbon, Cs is also a more effective promoter than K.⁹

The most intriguing aspect of this study is the promotional effect alkaline-earth cations like Ca and Ba have on catalysis by intrazeolitic Ru. Earlier work indicated that Ba and Cs are similarly effective promoters for Ru/carbon catalysts.¹⁰ However, as shown in Table 2, Ru/BaX and Ru/CaX are three times more active than Ru/CsX. To the best of our knowledge, the alkaline-earth zeolite catalysts discussed here are the most active zeolite-supported catalysts for ammonia synthesis reported to date. As shown in Table 2, the reactivity results for a second catalyst batch containing Ba cations, Ru/BaX(2), demonstrate that the high activity of Ru clusters supported on alkaline-earth zeolites is reproducible. The location of the alkaline-earth cations relative to the metal clusters are unknown at this time, but we expect that the cations reside at typical ion exchange sites as described by Breck.

Cisneros and Lunsford explained the reactivity trends for ruthenium clusters supported on zeolites by ranking the catalysts according to the partial charge on their framework oxygen atoms.⁵ Presumably, the negatively charged oxygen atoms donate some of their excess charge to the ruthenium clusters. The intermediate Sanderson electronegativity of the support was used to evaluate the partial oxygen charge of the zeolites.⁵ Table 2 shows the analogous calculations for our samples. As expected, the MgO sample has the greatest partial negative charge on the oxygens (lowest support electro-

negativity). Among the zeolite catalysts, however, the alkaline-earth zeolites have the least negatively charged framework oxygens but the greatest catalytic activities, even exceeding that of Ru/MgO. These surprising results suggest that local elemental composition in the vicinity of the ruthenium clusters must dominate the promotion of zeolite-supported Ru. Thus, global calculations of partial oxygen charge based on unit-cell compositions cannot account for the observed trend in ammonia synthesis activity.

This work points to a new direction in catalysis research that involves modification of nanometre-sized metal clusters with alkaline-earth cations in zeolites. Since the activation energy for ammonia synthesis is essentially constant for our series of materials, one speculation is that the addition of alkaline-earth ions to zeolite-supported Ru may actually increase the number density of active sites. However, the major advantage of the new ruthenium catalyst is that the metal clusters are supported on a well defined, crystalline zeolite that does not undergo oxidation or methanation like the amorphous carbon support used previously.

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Table 2 Effect of catalyst support on ammonia synthesis rate

Catalyst	TOF at 623 K ^a /10 ⁻⁴ s ⁻¹	E _a /kJ mol ⁻¹	S _{int} ^b	δ _O ^c
Ru/KX	1.91	106	3.22	-0.42
Ru/CsX	4.85	106	3.16	-0.43
Ru/CaX	14.9	102	3.55	-0.35
Ru/BaX	14.1	91	3.54	-0.35
Ru/BaX(2)	18.1	108	3.63	-0.33
Ru/MgO	10.5	94	2.85	-0.50

^a Turnover frequency of reaction based on number of surface Ru atoms counted by hydrogen chemisorption. ^b Intermediate Sanderson electronegativity of the support. ^c Average partial oxygen charge of the support.

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