Reusability of Silica-Supported vs Homogeneous Rh(III), Ir(III) and Ru(II) NHC complexes in catalysis

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Introduction

To date, numerous inorganic chemists, especially those focussing on the field of catalysis, are still heavily reliant on the use of the platinum group metals (PGM's), with the auto-catalysis industry still presenting as one of the main employers of these PGM-based catalysts. Given PGMs estimated lifespan of ca. 200 years, finding alternative methods of use are required especially to improve catalyst recyclability or reusability[1]. Heterogenisation presents an avenue through which these traditionally homogeneous catalysts can be made more reusable, by means of supporting them onto supports, typically silica-based. Coal fly ash (CFA), a by-product of coal combustion, primarily consists of SiO_2 (ca. 50%), making it an ideal feedstock for silica nanoparticle production[2].

Materials and Methods

The synthesis of amorphous mesoporous silica nanoparticles from a CFA-derived Na_2SiO_3 solutions was performed as previously reported[3]. A novel silica-containing NHC ligand was designed to allow for the immobilisation of the relevant Rh(III), Ir(III) and Ru(II) complexes. This was followed by the heterogenisation of these silyl tethered complexes onto silica nanoparticles. A secondary NHC ligand, featuring an isopropyl group instead of a silane group, was also synthesized and coordinated to the same metal precursors to serve as homogeneous catalyst counterparts to allow for the comparison of catalytic results. The homogeneous complexes were characterised by means of HR-MS and NMR spectroscopy, whereas the immobilised complexes were characterised by means of TGA, TEM. SEM-EDS and FTIR analysis.

Results and Discussion

The relevant results from the catalytic transfer hydrogenation, hydrolysation as well as the reusability studies of the appropriate complexes will be presented.

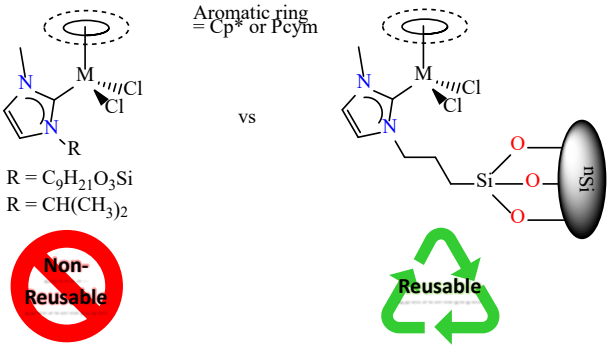

Figure 1: Homogenous vs heterogeneous NHC-based complexes

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Ruthenium complexes of pyrazolyl-pyridine complexes as catalyst precursors for formic acid dehydrogenation

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Hydrogen is a clean and renewable energy store, which provides an attractive alternative to fossil fuels.[1] Significant research efforts have been geared toward developing efficient hydrogen carriers. To this end, formic acid has emerged as the carrier of choice due to its favorable properties, which includes high hydrogen content by weight, ease of transport and handling.[2] The research efforts of the Swarts Research Group focus on the development of catalyst systems derived from earth-abundant metals.[3] Recent efforts in our group has been geared toward the development of new ligand scaffolds with tunable steric and electronic properties which can be exploited in catalysis. Herein, we report on a series of pyridine-pyrazolyl Ru(II) complexes bearing different electronic and steric properties as catalysts in formic acid dehydrogenation (**Figure 1**). The complexes, upon activation with formate, showed activity towards the dehydrogenation of FA to produce H_2 and CO_2. Optimisation of the various reaction conditions revealed the influence of temperature, solvent, substrate concentration and the nature and amount of formate additives on the activity of the catalyst. We demonstrated that the catalyst could dehydrogenate formic acid to CO_2 and H_2 in quantitative yields within 1 hour (5 mmol FA, 0.005 mmol catalyst loading, 3 mmol HCOOK, 100°C, DMSO) with TON's and TOF's of ~1030 and ~1230 h^{-1} respectively. Preliminary mechanistic studies also revealed the formation of hydride complex in the catalytic cycle.

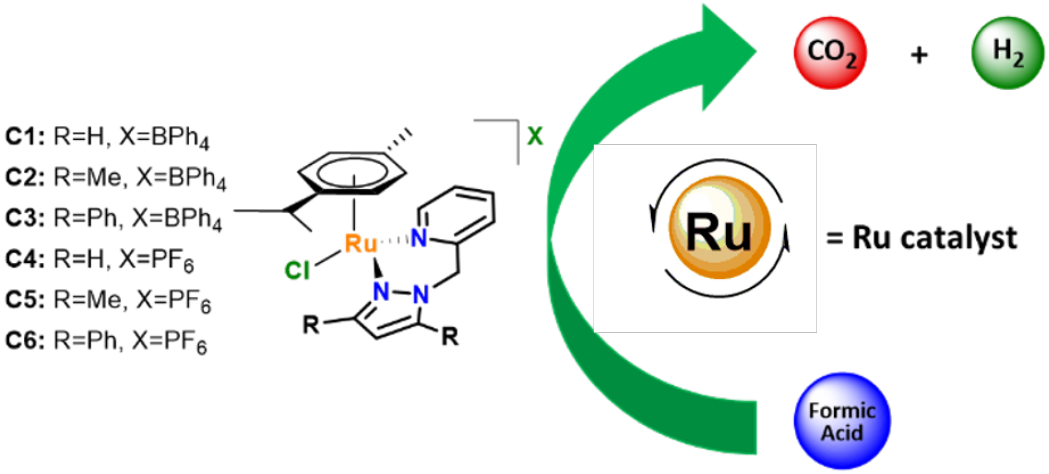

Figure 1: Formic acid dehydrogenation catalysed by Ru(II) pyridine-pyrazolyl complexes

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From Waste to Functional Material: Synthesis of Alumina Nanoparticles from Coal Fly Ash

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Introduction

Coal fly ash (CFA) is a by-product produced by the burning of pulverised coal to generate electricity. Utilisation of CFA as feedstock for the production of value-added products is crucial in mitigating the environmental impact of coal-based power plants. South African CFA contains more than 30 wt.% Al_2O_3,[1] making it an ideal candidate as precursor for synthesis of Al_2O_3 nanoparticles for applications in sorption[2] and catalysis[3].

Materials and Methods

Three synthetic techniques (sol-gel synthesis; hydrothermal synthesis; co-precipitation) were used to synthesise Al_2O_3 nanoparticles from CFA as well as commercial precursors, and their purity and porosity were compared. Various characterisation techniques (XRF, XRD, FTIR, EDX) were employed to characterise the nanoparticles. Their morphology was identified using SEM and TEM and their specific surface area and porosity were determined using BET surface area analysis.

Results and Discussion

Among the three synthetic techniques, hydrothermal synthesis produced nanoparticles with higher purity when using CFA leachates as the precursor, whereas co-precipitation achieved the highest purity with commercial precursors (Table 1). SO_3 was identified as the primary impurity in all samples. Although co-precipitation with commercial precursors resulted in the largest BET surface area, products synthesised from CFA leachates via the sol-gel and hydrothermal methods exhibited higher surface areas than those produced from commercial chemicals. These findings suggest that hydrothermal synthesis using CFA leachates is the best approach, yielding cost-effective products with good porosity for applications in sorption and catalysis. FTIR analysis confirmed the presence of hydroxyl groups in all products, making them suitable for further modification, such as complexation and silane coupling, for catalytic applications.

Table 1. Purity and BET surface area of synthesised Al_2O_3 nanoparticles.

Synthesis technique	Precursors	Purity (%)	BET surface area (m^2/g)
Sol-gel	Commercial	85	139
	CFA	82	186
Co-precipitation	Commercial	92	348
	CFA	72	135
Hydrothermal	Commercial	81	72
	CFA	88	259

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Bathochromic shifts in Cu(β-diketonato)$_2$ complexes for DSSC

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Introduction

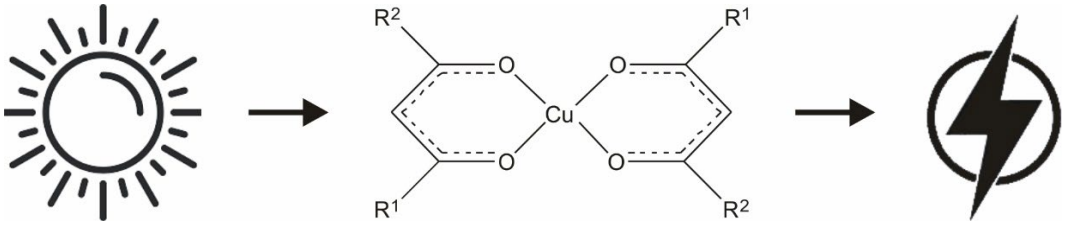
Rising global electricity demand, driven by population growth, is challenging due to diminishing fossil fuel resources.[1] Silicon-based solar cells offer an eco-friendly alternative but face issues like complex manufacturing, hazardous materials, and high costs.[2] This has led to the development of low-cost dye-sensitized solar cells (DSSCs), which convert sunlight into electricity using dyes, electrolytes, photoanodes, and counter electrodes.[3,4] As a third-generation photovoltaic technology, DSSCs are sustainable, reduce greenhouse gas emissions, and provide energy independence, especially in remote areas. They operate efficiently under various lighting conditions using natural, organic, and inorganic dyes.[5]

Materials and Methods

DFT calculations were conducted on the neutral molecules with multiplicity 2, using the PBEh1PBE functional and the aug-cc-pVDZ basis set as implemented in the Gaussian 16 package. The molecules were all optimized in the solvent phase (acetonitrile), using the IEFPCM.

Results and Discussion

Copper, a plentiful and non-toxic metal, is a promising, cost-effective alternative to the commonly used ruthenium in DSSCs. This study presents DFT-calculated UV/Vis properties for 11 Cu(β-diketonato)$_2$ complexes, featuring β-diketonato ligands with zero, one or two aromatic rings. Experimentally, absorbance maxima range from 295-390 nm, while calculated values span 302-425 nm. More aromatic rings result in bathochromic shifts, moving absorbance maxima from the UV toward the visible region. Complexes without aromatic rings show ligand-to-metal charge transfer, while those with one or two rings exhibit ligand-to-ligand charge transfer.



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