

Hydrogenation of olefins on Ru/pillared montmorillonite

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Abstract. Hydrogenation reactions of olefinic hydrocarbons using ruthenium-incorporated pillared montmorillonite as catalysts are reported. Depending on the steric hindrance, Ru/pillared montmorillonite selectively reduces carbon-carbon double bonds using hydrogen under pressure.

Keywords. Clay catalysis; Ru/pillar; hydrogenation; olefins; montmorillonite.

1. Introduction

There is much interest in clay catalysts and catalyst supports (Pinnavaia 1983). Expandable layer lattice clays such as montmorillonite exhibit Hammett acidity function values between 1.5 and -3 in their naturally occurring forms, which have been reported in a number of proton-assisted reactions of organic molecules using such clay types (Ballantine *et al* 1981; Laszlo 1987). The objective of making pillared clays is to achieve as large a basal spacing as possible. Large surface area and porous volume, which can be achieved from large basal spacings, are the main requirements of an acceptable catalyst (Plee *et al* 1987). Intercalated species giving rise to stable basal spacing have been characterized by small angle X-ray scattering (Raush and Bale 1964). The spectral differences between adsorbed enantiomers and racemic chelates are general features for all the clays (Joshi *et al* 1986, 1988, 1990; Kamat *et al* 1991). These studies tell us more about the binding states of the enantiomeric and racemic forms. The unusual intercalation properties of polypyridyl and the resolution of racemic mixtures of several Ru(II) complexes on chirally modified column is reported (Kotkar *et al* 1986; Kotkar and Ghosh 1987). This has stimulated our interest in this area.

We note here our previous work in this direction on cyclodehydration of non-aromatic diols catalysed by Al-montmorillonite (Kotkar and Ghosh 1986; Kotkar *et al* 1988). Palladium complexes anchored in montmorillonite used as catalysts in selective hydrogenation of alkenes have been synthesised and studied (Choudary *et al* 1985, 1991).

The aim of the present work was to prepare Ru/pillared montmorillonite catalysts from enantiomeric and racemic forms of the complex, which may give rise to variations in organic reactions. But our observations show no difference in the product formation between enantiomeric and racemic forms of ruthenium complex. We report here the hydrogenation of olefins using the racemic form of the ruthenium complex incorporating pillared montmorillonite as a catalyst.

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2. Experimental

2.1 Catalyst preparation

The clay was converted into its Na-exchanged form by mechanical stirring in 2M NaCl (50 ml/g of clay) at room temperature for 4–5 days. This was followed by repetitive high speed centrifugation and redispersion of residue in water. Finally the clay dispersion was centrifuged to remove heavier particles. The strength of clay dispersion obtained was 20 g/l. Chloride salts of $\text{Ru}(\text{phen})_3^{2+}$ (phen = 1, 10 phenanthroline) were synthesized according to the procedure reported in literature (Braddock and Meyer 1973). $[\text{Ru}(\text{phen})_3]\text{Cl}_2$ was converted into perchlorate by addition of sodium perchlorate. 10 ml of an aqueous solution containing 126 mg $\text{Ru}(\text{phen})_3(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ was added into ≈ 50 ml of an aqueous Na–montmorillonite dispersion containing 20 g/l clay. The contents were stirred overnight and the clay was centrifuged to remove excess water. The clay slurry containing the Ru(II) complex was next added to ≈ 560 ml of an aqueous solution of pillaring agent. The pillaring agent was prepared by gradually adding 480 ml of 0.05 M NaOH into 100 ml of 0.1 M AlCl_3 and stirring for an hour at 50°C at which point a clear solution was formed. The Ru(II)/clay dispersion modified with pillaring agent was centrifuged and washed six times with distilled water and air-dried at 80°C. The catalyst precursor, namely $\text{Ru}(\text{phen})_3^{2+}$ in the form of dry clay mass, was then crushed into a powder and calcined at 425°C for 4 h in air. This was subsequently reduced at 300°C under a flow of hydrogen for 8 h to yield Ru(0) as the catalytically active species. A known amount of catalyst was digested in aqua regia for 16 h and filtered. The filtrate was quantitatively made up to a known volume. The Ru content in this solution was measured by atomic absorption spectroscopy. Within limits of experimental errors the value so obtained matched with the theoretical value (1.7%).

2.2 Reaction conditions

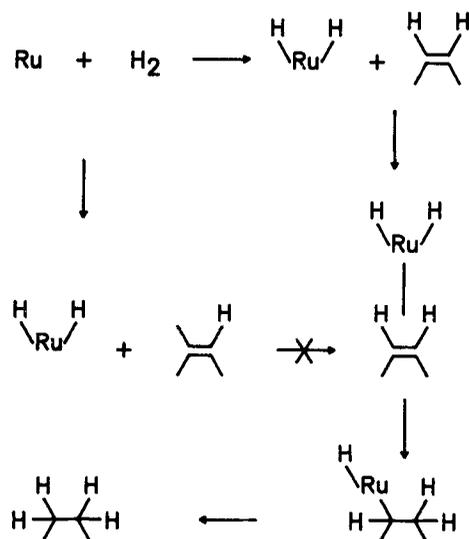
All the reactions were carried out in a 100 ml capacity Parr autoclave at 100°C. Typically, 60 mg of catalyst and 5 ml of reactant were charged with 200 psi of hydrogen at room temperature. The autoclave was purged with hydrogen before charging at room temperature. The reaction was carried out for 17 h.

3. Results and discussion

It was found in the present work that ruthenium-incorporated pillared montmorillonite catalyses the hydrogenation of various cycloalkenes to the corresponding cycloalkanes. Cyclohexene was hydrogenated to cyclohexane up to 56% (table 1). Whereas 1-methyl-1-cyclohexene was recovered unchanged under similar conditions due to steric hindrance, 2-cyclohexene-1-one was converted into cyclohexanone, albeit at a slower rate compared to cyclohexene, while cyclohexanone did not get reduced, indicating the selectivity of Ru/pillared montmorillonite for olefin double bonds over the carboxy group. However, the difference in the bond energy between the carbon–carbon double bond (598 kJ mol^{-1}) and the carbon–oxygen double bond (695 kJ mol^{-1}) explains the reason for the observed selectivity in this system. The catalytic hydrogenation experiments for some of the substrates depicted in table 1 have been carried out at an elevated temperature of 180°C. Even then one fails to observe the hydrogenation of the ketone functional group. The hydrogenation is thus selective to the olefin function.

Table 1. Hydrogenation reactions of olefins catalysed by ruthenium incorporated pillared montmorillonite.

Reactant	% Unreacted	Major product	Yield %
	44		56
	100	-	-
	46		53
	100	-	-
	34		50
	100	-	-
	100	-	-

**Scheme 1.**

Hydrogenation reactions with unsaturated aldehydes were also attempted. No reaction was observed with 3-methyl crotonaldehyde and 4-methyl-3-pentene-2-one, while crotonaldehyde gave a mixture containing a major product with 50% butyraldehyde (table 1). Expectedly, butyl alcohol was not produced as confirmed by gas chromatography. The formation of unidentified products has led us to conclude that rearrangement reactions occur to some extent in this system. The orientation of the substrate towards the catalyst could be as shown in scheme 1, which also indicates that the energy required would be more after the replacement of hydrogen with a methyl group. Hence no reaction was observed with 1-methyl-1-cyclohexene and 4-methyl-3-pentene-2-one, and there was no consumption of hydrogen observed in the autoclave during the reaction. We note that competition in hydrogenation of cycloalkenes over Rh/montmorillonite has been studied, results of these studies are being reported elsewhere (Thakkar *et al* 1994).

4. Conclusion

In conclusion, our studies indicate that Ru/pillared montmorillonite selectivity reduces carbon-carbon double bonds using hydrogen under pressure. The reaction depends on steric factors, with substrates having bulkier groups not reacting.

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