Hydrogenation of cycloalkenes on Rh/montmorillonite

DILIP KOTKAR and N V THAKKAR*

Inorganic Chemistry Division, The Institute of Science, 15, Madam Cama Road, Mumbai 400 032, India

Abstract. We report here the hydrogenation of cycloalkenes using Rh-supported montmorillonite as a catalyst. The catalyst preparation was based on oxidative degradation of intercalated *tris*(phenanthroline)–Rh (III) followed by reduction under hydrogen atmosphere. No obvious trend is seen in the hydrogenation yields of the olefins though cyclopentene and cyclooctene are reduced faster than cyclohexene and cycloheptene. 2-Cyclohexen-1-one reacts marginally faster than cyclohexene under similar conditions. When the hydrogenation experiments were repeated employing binary mixtures of the olefins, considerable differences in hydrogenation behaviour were observed over that found when the olefins were taken in their pure form. The most notable difference in the hydrogenation behaviour of binary mixtures was observed in the case of cyclopentene/cyclooctene: both olefins could be efficiently hydrogenated in their pure form but there was no conversion of cyclooctene in presence of cyclopentene.

Keywords. Cycloalkene; binary mixture; hydrogenation; rhodium; montmorillonite.

1. Introduction

Polypyridine complexes of transition metals such as Ru, Fe, Os, Rh and Cr have been under active investigation (Creutz *et al* 1980). Layered materials offer two-dimensional expandable interlayer space for accommodating guest species (Whittingham and Jacobson 1982). Various layered materials such as clay minerals, metal phosphates and transition metal oxides have been known as host materials for intercalation compounds. On this basis, intercalation compounds have been studied as catalysts and their supports (Pinnavaia 1983). Molecular recognition and substrate selectivity in the hydrogenation of olefins have been studied with Pd catalyst (Choudary *et al* 1990; Choudary and Rao 1992).

Our interest in this approach towards catalyst synthesis originated from previous studies by Ghosh and coworkers on the spectral properties of intercalated poly (pyridyl) Ru (II) chelates adsorbed on smectite clays (Joshi *et al* 1986; Joshi and Ghosh 1987, 1989; Kamat *et al* 1991). Previous work by the authors on clay-catalysed organic reactions is noted (Kotkar and Ghosh 1986; Kotkar *et al* 1988; Kotkar and Thakkar 1995).

We report here the hydrogenation of cycloalkenes using Rh-incorporated montmorillonite as a catalyst. The effect of oxidation, reduction and alternating oxidation/reduction treatments on the oxidation state and the morphology of silica supported Rh catalysts have been studied (Wong and McCabe 1987). In our studies, hydrogenation experiments were carried out using binary mixtures of the olefins;

---

* For correspondence

considerable differences in hydrogenation behaviour were observed. The stereochemistry of cycloalkene hydrogenation depends on the chemical and steric structure of the substrates, catalysts and reaction conditions (Mitsui *et al* 1973).

2. Experimental

2.1 *Catalyst preparation*

Montmorillonite from Wyoming bentonite (GK 129, Georgia Kaolin Co) was employed in the present work. The clay was converted into its Na^+-exchanged form by mechanical stirring in 2 M NaCl (40 ml/g of clay) at room temperature for 4–5 days. This was followed by repetitive high-speed centrifugation on a REMI centrifuge (Model R-24) and redispersion of the residue in water. Finally the clay dispersion was centrifuged for 30 min (5000–6000 rpm). The strength of the clay dispersion (18 g/L) was determined by drying a known volume of a dispersion on a glass slide and measuring the weight of the residue. An aqueous solution (10 ml) containing $[Rh(phen)_3]Cl_3 \cdot 3H_2O$ (phen = 1,10 phenanthroline) (336 mg) was added to 220 ml of an aqueous Na-montmorillonite dispersion containing 18 g/l clay. The contents were stirred overnight and the clay was then centrifuged to remove excess water. The Rh(III)-containing clay slurry was next added to 120 ml of the aqueous pillaring solution (Plee *et al* 1987). The pillaring solution was prepared by adding gradually 80 ml of 0·4 M NaOH into 40 ml of 0·4 M $Al(NO_3)_3$ and stirring for 1 hour at 50°C at which point a clear solution was formed.

The Rh(III)/clay dispersion modified with pillaring agent was centrifuged, washed six times with distilled water and then air dried at 80°C. The catalyst precursor, namely $Rh(phen)_3^{3+}$ in the form of dry clay mass, was then crushed into a powder and calcined at 450°C for 4 hours in air. This was subsequently reduced at 350°C under a flow of hydrogen for 8 hours. A known amount of catalyst was digested in aqua regia for 16 hours and filtered. The filtrate was quantitatively made up to a known volume. The Rh content in this solution was measured by atomic absorption spectroscopy (GBC Model 932). The value so obtained (1.5%) matched the theoretical value.

The X-ray diffraction (XRD) analysis was carried out using Philips diffractometer with CuKα radiation (figure 1).

2.2 *Apparatus and procedures*

A 100 ml thermostated Parr autoclave was charged with the reactant (5 ml), rhodium montmorillonite catalyst (100 mg) and with 200 psi of hydrogen at room temperature. The autoclave was purged with hydrogen before charging at room temperature. The autoclave was then heated at 100°C for 20 hours. The reaction mixture was then cooled, separated from the catalyst and analysed by GC. GC analysis was carried out on a Hewlett–Packard model 5890 gas chromatograph using FID and HP-101 column.

Hydrogenation experiments of binary mixtures of the olefins were carried out in 100 ml Parr autoclave. The amount of catalyst was 100 mg whereas the amount of each reactant taken was 0·06 moles (table 1).

3. Results and discussion

Catalyst preparation was based on oxidative degradation of intercalated *tris* (phenanthroline) Rh (III) followed by reduction under hydrogen. The objective in pillaring clay
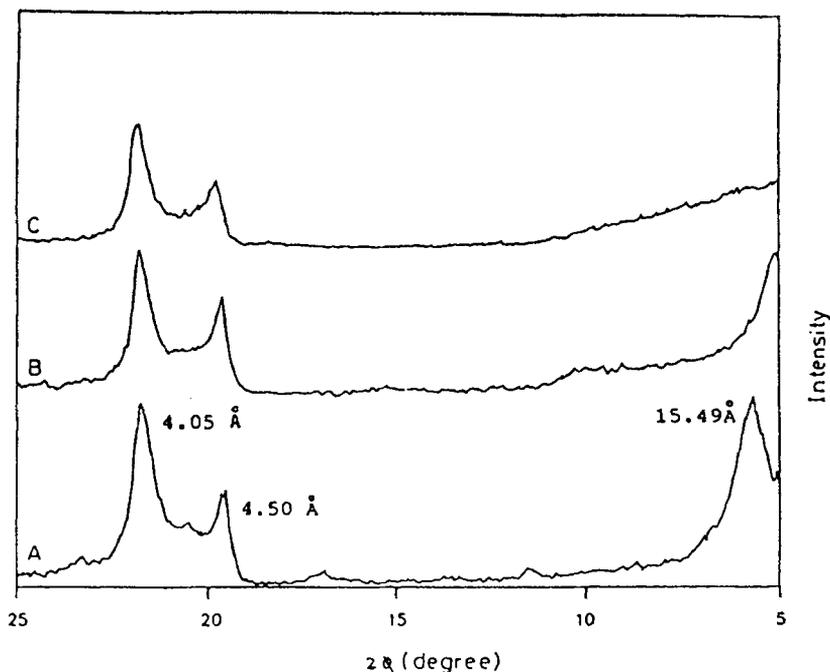
Figure 1. XRD patterns of clay (A), pillar clay (B) and rhodium pillar clay (C).

Table 1. Competition in hydrogenation of cycloalkenes over Rh/montmorillonite.

Entry	Reaction mixture[b] (GC%)[a]	Time (h)	Product mixture (GC%)[a]	
1	Cyclohexene (33·6) + Cyclooctene (59·8)	5·5	Cyclohexene + Cyclohexane (28·5) (4·1) + Cyclooctene + Cyclooctane (56·3) (1·29)	
2	Cyclohexene (33·6) + Cyclooctene (59·8)	20	Cyclohexene + Cyclohexane (12·6) (21·0) + Cyclooctene + Cyclooctane (49·3) (7·2)	
3	Cyclopentene (38·3) + Cyclooctene (58·0)	20	Cyclopentene + Cyclopentane (16·0) (20·8) + Cyclooctene + Cyclooctane (56·8) (0·0)	

[a]GC analysis (actual % given in parentheses)
[b]The catalyst amount was 100 mg whereas the amount of each reactant was 0·06 moles. Catalyst:substrate ≈ 1:4000.

is to achieve as large a basal spacing as possible. Large basal spacing contributes to the development of large surface areas and porous volumes which are the main requirements for acceptable catalysts. The XRD analysis of catalyst showed that there is no change at higher angles when pillared montmorillonite and Rh-pillared montmorillonite were compared with montmorillonite itself (figure 1). However, at lower angles the distance observed (15·49 Å) in montmorillonite with the corresponding peak was shifted to lower angles in pillared clay and was further shifted to the lowest angles in Rh-pillared clay. This indicates that there is an expansion of the interlayer spacing in montmorillonite after pillaring but Rh-pillar clay shows reduction in the intensity of the reflection peak, compared to the clay peak.

3.1   *Hydrogenation of cycloalkenes*

Table 2 provides data on the hydrogenation of a range of cycloalkenes. Curiously, there is no obvious trend in the hydrogenation yields of the olefins, cyclopentene and cyclooctene being reduced faster than cyclohexene and cycloheptene. These variations are, therefore, not on account of any size selectivity of the catalyst. The heats of hydrogenation (ΔH) of the cycloalkenes (C5–C8), are different from one another (Ermer and Lifson 1973). This supports the variation that we have observed in the hydrogenation yields of cycloalkenes. The orientation of the substrate towards the catalyst could be interpreted on the basis of the Horiuti–Polanyi mechanism (Horiuti and Polanyi 1934).

Table 2.   Hydrogenation reactions of cycloalkenes catalysed by rhodium incorporated montmorillonite[a].

No.	Reactant	% Unreacted	Major product	GC Yield %
1		3		96
2		23		68
3		21		71
4		23		66
5		0		98

[a] All the reactions were carried out for 20 h with 5 ml of reactant and 100 mg of catalyst:substrate $\approx$ 1:4000

It was observed that (table 2) 2-cyclohexen-1-one was converted into cyclohexanone, albeit at a higher yield compared to cyclohexene. Expectedly, cyclohexanol was not produced as confirmed by GC. The presence of the CO group imparts some polarity difference in the vicinity of the C = C that shows higher yield compared to cyclohexene. We have found some small amounts of unidentified products in the hydrogenation of cyclohexene and cycloheptene. The formation of unidentified products has led us to conclude that rearrangement reactions occur to some extent in this system.

3.2 *Competition in hydrogenation of binary mixtures of cycloalkenes*

Equimolar amounts of cyclopentene and cyclooctene as well as cyclohexene and cyclooctene were mixed and kept ready for the experiments (table 1). Experiments were carried out for 20 hours, however, the cyclohexene/cyclooctene reaction was carried out for 5·5 h for measurement of the initial hydrogenation yield of the binary mixture system, which indicated a higher hydrogenation yield for cyclohexene than for cyclooctene.

When the hydrogenation experiments were repeated employing binary mixtures of the olefins, considerable differences in hydrogenation behaviour were observed from that observed when the olefins were taken in their pure form. For example, while cyclooctene could be hydrogenated somewhat more efficiently than cyclohexene (table 2), the binary mixture system indicated a higher hydrogenation yield for cyclohexene than for cyclooctene. In the hydrogenation reaction of a binary mixture system the reactants, therefore, independently hydrogenate to yield a saturated product mixture. The most notable difference in the hydrogenation behaviour of binary mixtures was observed in the case of cyclopentene/cyclooctene. Thus, while in pure form both olefins could be efficiently hydrogenated, there was no conversion of cyclooctene in presence of cyclopentene. On the other hand, the hydrogenation rate of cyclopentene was retarded significantly in presence of cyclooctene. It can be interpreted that a mixture of cyclopentene/cyclooctene rings exert a shielding effect on the adsorption of the molecule. However, only free cyclopentene molecules converted to cyclopentane as a product. It was suggested that, for hydrogen addition to take place to the olefinic double bond, the active centre must have proper geometry which is illustrated in the reference (Bartok 1985). Cyclohexene/cyclooctene hydrogenation behaviour was observed with some inhibition in product formation.

4. Conclusion

In conclusion, it is demonstrated in this work that the hydrogenation behaviour of cycloalkenes can differ quite significantly depending upon whether the alkene is present in pure form or as a mixture. The results suggest that factors other than size/shape selectivity of catalyst can impart differences in yields of hydrogenation of cycloalkenes even though such differences in yields may not be apparent for the olefins in their pure forms.

References

Bartok M 1985 *Stereochemistry of heterogeneous metal catalysts* (Chichester, New York, Brisbane, Toronto, Singapore: Wiley-Interscience) p. 171

Choudary B M and Rao K K 1992 *Tetrahedron Lett.* **33** 121

Choudary B M, Sarma M R and Rao K K 1990 *Tetrahedron Lett.* **31** 5781

Creutz C, Chou M, Netzel T L, Okumura M and Sutin N 1980 *J. Am. Chem. Soc.* **102** 1309

Ermer O and Lifson S 1973 *J. Am. Chem. Soc.* **95** 4121

Horiuti J and Polanyi M 1934 *Trans. Faraday Soc.* **30** 1164

Joshi V and Ghosh P K 1987 *J. Chem. Soc., Chem. Commun.* 789

Joshi V and Ghosh P K 1989 *J. Am. Chem. Soc.* **111** 5604

Joshi V, Kotkar D and Ghosh P K 1986 *J. Am. Chem. Soc.* **108** 1987

Kamat P V, Gopidas K R, Mukherjee T, Joshi V, Kotkar D, Pathak V S and Ghosh P K 1991 *J. Phys. Chem.* **95** 10009

Kotkar D and Ghosh P K 1986 *J. Chem. Soc., Chem. Commun.* 650

Kotkar D and Thakkar N V 1995 *Proc. Indian Acad. Sci. (Chem. Sci.)* **107** 39

Kotkar D, Mahajan S W, Mandal A K and Ghosh P K 1988 *J. Chem. Soc., Perkin Trans. I* 1749

Mitsui S, Senda Y, Suzuki H, Sekiguchi S and Kumagai Y 1973 *Tetrahedron* **29** 3341

Pinnavaia T J 1983 *Science* **220** 4595

Plee D, Gatineau L and Fripiat J J 1987 *Clays Clay Miner.* **35** 81

Whittingham M S and Jacobson A J (eds) 1982 *Intercalation chemistry* (New York: Academic Press)

Wong C and McCabe R W 1987 *J. Catal.* **107** 535