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A4.2

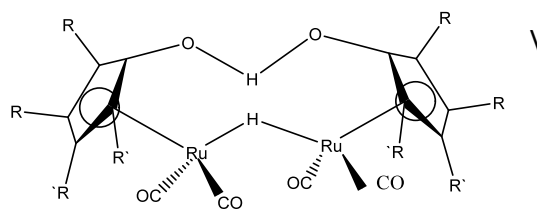
Reduction of Cyclohexanols and Cyclohexanone in waste Streams to Cyclohexane is a type of Hydrogen Transfer Reduction (HPR). It is an elegant way of reduction because it does not require the use of hydrogen pressure which require special equipment. In the presence of Hydrogen donors like H₂, Isopropanol, Formic acid derivatives like Sodium Formate etc. Cyclohexanone can be reduced to cyclohexanol and then to cyclohexane by a variety of transition metal Catalysts. Of these **Ruthenium (Ru), Rhodium(Rh) catalysts** are most effective. Infact, the Hydrogen donors are the Reducing Agents in HPR.

NaHCO₂ as Reducing agent:

Cyclohexanone and Cyclohexanol can be reduced by Sodium Formate (NaHCO₂) using catalyst like 1:10 mixture of RhCl(PPh₃)₃ & PPh₃. Here, Sodium Formate is acting as Hydrogen donor for this reaction. This reaction is done under the presence of Aliquat-336. So, this catalysis is an eco-friendly reaction. Presence of Aliquat-336 will enhance the reactivity towards Ketones than Aldehydes. For Cyclohexane, Aliquat-336 will be useful. This reaction is more selective in Basic medium. The pH range should be in between 9 to 11.

Another Ruthenium complex ($\eta^5\text{-C}_4\text{Ph}_4\text{COHOC}_4\text{Ph}_4\text{-}\eta^5$) ($\mu\text{-H}$) (CO)₄Ru₂ and its phenyl ring-substituted derivatives were found to act as efficient catalysts in reduction reactions of Cyclohexanone and Cyclohexanol to Cyclohexane using Sodium Formate as Hydrogen source.

The Catalysts are characterized by ¹H NMR, ¹³C NMR before and after the reaction. Raman Spectroscopic technique is used for characterizing the catalyst during the reaction.



($\eta^5\text{-C}_4\text{Ph}_4\text{COHOC}_4\text{Ph}_4\text{-}\eta^5$) ($\mu\text{-H}$) (CO)₄Ru₂ Complex

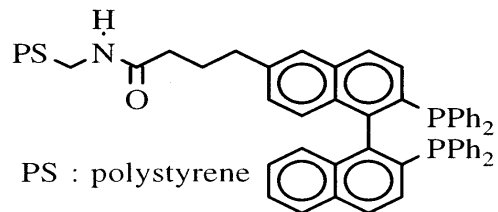
Iso Propanol as Reducing Agent:

Using Isopropanol (IPO) as reducing agent, Cyclohexanone and Cyclohexane can be reduced to Cyclohexane by the Transition metal Catalysts especially Ruthenium (Ru) complexes. Here, Isopropanol is acting as Hydrogen donor for the catalyst. [Ru(benzene)Cl₂]₂ complex can effectively catalyse this Hydrogen Transfer Reduction. Polymeric ligand coordinated Ruthenium complexes will also catalyse this reduction. Ligands like BINAP, NORPHOS, CHIRAPHOS etc. can be used. Of these BINAP is more effective. (BINAP-RuBr₂ complex)

The Catalysts are characterized by ^1H NMR, ^{13}C NMR before and after the reaction. Raman Spectroscopic technique is used for characterizing the catalyst during the reaction.

Rhodium complex generated in situ from $[\text{Rh}(\text{COD})\text{Cl}]_2$ and triphenylphosphine trisulfonate ($\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$, TPPTS) can also be a quite effective catalyst for transfer hydrogenation of aldehydes and ketones with isopropanol, under basic conditions.

Here, COD is Cyclooctadiene.

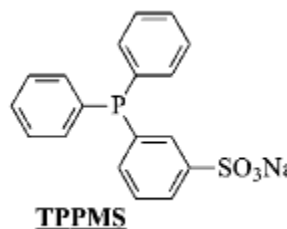
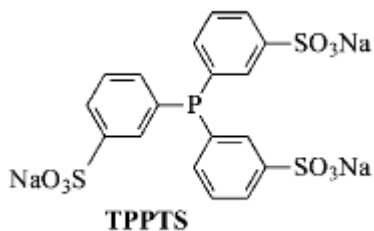


Bayston's heterogenized BINAP

H₂ as Reducing Agent:

Using Hydrogen as reducing agent, reduction can be carried out on Platinum Surface (Pt) as catalyst. Raney Nickel (Ni) can also be used for this reduction process. These processes require high temperatures and pressures. For these catalysts, Powder-X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) techniques are used to characterize the catalyst before and after the reaction. Raman Spectroscopic Technique is used for characterizing catalyst during the reaction.

Apart from these methods, there are other Ru, Pd transition metal complexes catalyzed Hydrogen Transfer Reduction Processes. $[\text{Rh}(\text{COD})\text{Cl}]_2$ with TPPTS (TriPhenylPhosphine TriSulfonate) is used as a catalyst. Another catalyst is $\text{RhCl}(\text{TPPMS})_3$ where TPPMS is TriPhenylPhosphine MonoSulfonate.



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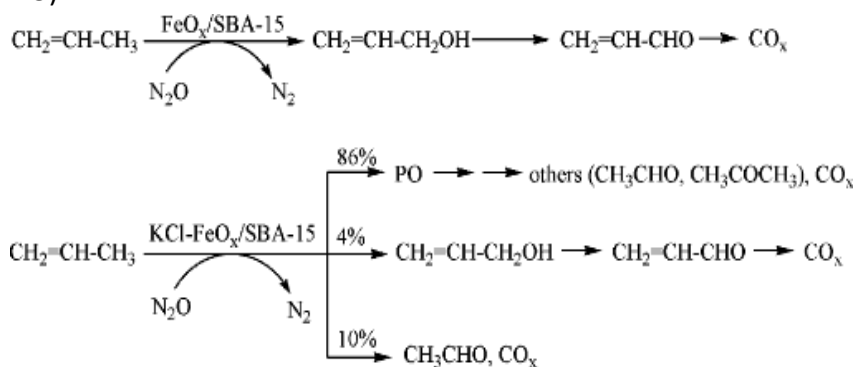
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A 4.3

Epoxidation of Propene to Propene Oxide using N_2O can be done effectively by using iron-based catalysts.

Heterogeneous Catalysts like **FeO_x supported Mesoporous Silica Nanoparticles (MSNs) like SBA-15** (Santa Barbara Amorphous type material) are effective heterogeneous catalysts for epoxidation of propene using nitrous oxide.

- When an FeO_x/SBA-15 catalyst was modified with alkali metal salts, the epoxidation of propene by N_2O could proceed with high selectivities and the modifier played a crucial role in determining the reaction route. Presence of the alkali metal salts not only enhances the selectivity to Propene oxide but also increases the C₃H₆ conversion and the turnover frequency (TOF) under the same reaction conditions. KCl was the best modifier for the conversion of C₃H₆ to Propene oxide by N_2O . PO selectivity and yield decreased with the following sequence, KCl > NaCl > RbCl > CsCl > LiCl.
- So, the catalyst used for epoxidation of Propene to Propene Oxide using Nitrous Oxide is **KCl-1 wt % FeO_x/SBA-15**. (K/Fe = 5)



- The decomposition of N_2O on active iron sites in the FeO_x-SBA-15 catalyst can generate active oxygen species (known as α -oxygen) responsible for the selective oxidation of Propene to Propene oxide. At elevated temperatures these catalysts are thought to yield surface activated iron-oxo species (α -oxygen), which are capable of oxygen transfer to Propene.
- Generation of Active Oxygen Species (α -oxygen) from N_2O on active iron sites of FeO_x-SBA-15 catalyst is the rate determining step in these catalysis. The nucleophilic lattice oxygen species associated with the iron species (FeO_x clusters) generally attack the allylic hydrogen and lead to allylic oxidation. But reactivity of lattice oxygen was inhibited by the modification of catalyst with KCl. Thus, the decrease in the reactivity of the lattice oxygen would suppress the allylic oxidation of propylene and lead to the formation of Propene Oxide.
- These hypotheses can be checked by several Spectroscopic techniques like H₂-TPR, UV-Vis, XANES, Powder-XRD and Raman spectroscopy.

- With KCl modification, the dispersion of iron species is further enhanced and the local coordination of iron is changed into a surface tetrahedral configuration, which probably accounts for the epoxidation of C_3H_6 by N_2O . Among these roles, the change of the local coordination structure of iron induced by KCl is believed to be the most important.

Other Methods:

Recent studies have shown that epoxidation of Propene by N_2O can also be done using catalysts like **KCl modified Fe-MFI and Fe-MCM-41**. These catalysts without modification with alkali salt (KCl) showed high activity in converting propene to acrolein and allyl alcohol. But after modification with KCl, they show selectivity towards Propene Oxide. These Catalysts have extra-framework iron species (e.g., FeO_x clusters) which is responsible for exhibiting higher Propene Oxide formation activity after modification. Highly dispersed extra-framework iron species, probably in tetrahedral coordination, are proposed for the epoxidation of propylene with nitrous oxide.

4.3 c)

KCl-1 wt % FeO_x/SBA-15 catalyst is not able for gas/liquid oxidation process to make phenol from benzene. The α -oxygen generated by decomposition of N_2O on the catalyst is not capable for this oxidation. The reason for this is :

For activation of N_2O on the catalyst, the iron species located in extra-framework positions are required. Activation of N_2O on the catalyst leads to formation of α -oxygen which is responsible for the oxidation of benzene to phenol. So, the catalyst should have extra- framework iron species.

But, if we use KCl/Fe-MFI and Fe-MCM-41 as catalyst, these can also catalyse the oxidation of benzene to phenol. Because these catalyst have extra framework positions in them. They have extra-framework Fe–O–Al pair sites where the α -oxygen will coordinate on activation of N_2O .

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