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Studies on Catalytic Properties of Mixed Oxides of Rare-Earth Transition Metals with special reference to LnMO_3 .

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Abstract: Mixed oxides of transition metals have gained significant attention due to their remarkable catalytic properties in various chemical reactions. Among these materials, perovskite-type oxides with the general formula LnMO_3 (where Ln = lanthanide element and M = transition metal) exhibit excellent catalytic activity, structural stability, and tunable electronic properties. These oxides have been widely studied for applications in oxidation reactions, fuel cells, environmental catalysis, and energy conversion processes. The catalytic behavior of LnMO_3 materials depends on factors such as the nature of the transition metal at the B-site, oxygen vacancies, redox properties, and structural distortions. In this study, the catalytic properties of mixed transition metal oxides with emphasis on LnMO_3 perovskites are reviewed and analyzed. Comparative catalytic performance, structural parameters, and reaction mechanisms are discussed using representative examples such as LaCoO_3 , LaMnO_3 , LaFeO_3 , and LaNiO_3 . The study highlights the importance of B-site cation selection and oxygen mobility in determining catalytic activity. The results demonstrate that LnMO_3 perovskites represent promising alternatives to noble metal catalysts due to their cost-effectiveness, thermal stability, and high catalytic efficiency.

Keywords: Perovskite oxides, LnMO_3 , mixed metal oxides, heterogeneous catalysis, transition metals, oxidation reactions

1. Introduction

Catalysts play a crucial role in accelerating chemical reactions without being consumed during the process. In heterogeneous catalysis, metal oxides represent an important class of catalysts because of their high stability, resistance to poisoning, and structural versatility. Among these materials, mixed oxides



containing transition metals have attracted considerable interest due to their tunable electronic structure and catalytic efficiency (Mabate et al., 2023).

Perovskite-type mixed oxides with the general formula ABO_3 represent one of the most important families of catalytic materials. In this structure, the A-site is usually occupied by a rare-earth element such as La, Nd, or Pr, while the B-site is occupied by a transition metal such as Mn, Fe, Co, or Ni. The structural flexibility of perovskites allows substitution at both A and B sites, leading to significant variations in catalytic properties (Zhu et al., 2015).

The catalytic activity of $LnMO_3$ oxides is largely governed by the transition metal present at the B-site. Studies have shown that B-site cations determine the redox behavior and catalytic activity, whereas the lanthanide ions mainly stabilize the crystal structure (Nitadori et al., 1988).

$LnMO_3$ perovskites have been investigated extensively for catalytic processes such as:

- CO oxidation
- Hydrocarbon oxidation
- Oxygen reduction reaction (ORR)
- Hydrogen evolution reaction (HER)
- Environmental pollutant degradation

These materials are particularly attractive because they can replace expensive noble metals such as platinum and palladium in many catalytic applications.

2. Structure of $LnMO_3$ Perovskite Oxides

The **perovskite structure** consists of a three-dimensional framework where the A-site cation is coordinated by twelve oxygen atoms, while the B-site cation is surrounded by six oxygen atoms forming an octahedral coordination. This arrangement forms a stable cubic or distorted cubic lattice.

General formula

$LnMO_3$

Where:

Component	Description
Ln	Lanthanide element (La, Nd, Sm, Pr etc.)
M	Transition metal (Co, Fe, Mn, Ni etc.)
O	Oxygen



The catalytic activity of perovskites arises mainly from:

- Oxygen vacancies
- Mixed valence states of transition metals
- High oxygen mobility
- Strong metal–oxygen interactions

The ability to substitute cations at both lattice positions enables the design of catalysts with optimized properties for specific reactions (Misono, 2013).

3. Catalytic Properties of LnMO_3 Oxides

3.1 Role of B-site Transition Metals

The nature of the transition metal strongly influences catalytic activity. Studies have demonstrated that perovskites containing Ni, Co, and Mn show higher catalytic performance due to their multiple oxidation states and redox activity (Zhu et al., 2015).

For example, **LaNiO_3 catalysts exhibit excellent activity for CO oxidation**, which has been attributed to reactive lattice oxygen and strong metal–oxygen bonding.

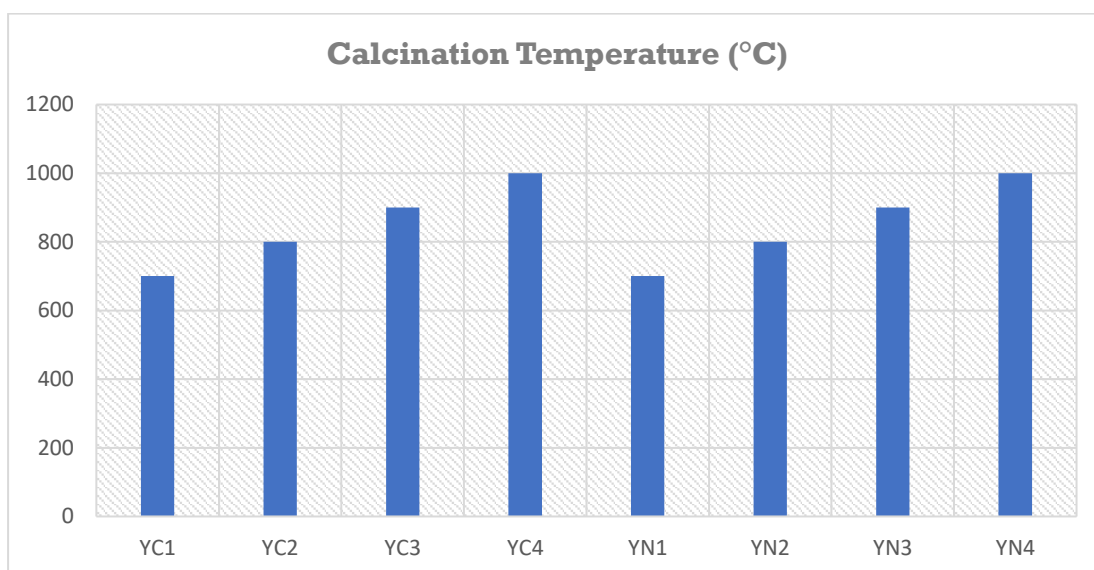
Table 1: Common LnMO_3 Perovskite Catalysts

Catalyst	Transition Metal	Main Catalytic Reaction
LaMnO_3	Mn	Oxygen reduction reaction
LaFeO_3	Fe	Hydrocarbon oxidation
LaCoO_3	Co	CO oxidation
LaNiO_3	Ni	CO and benzene oxidation

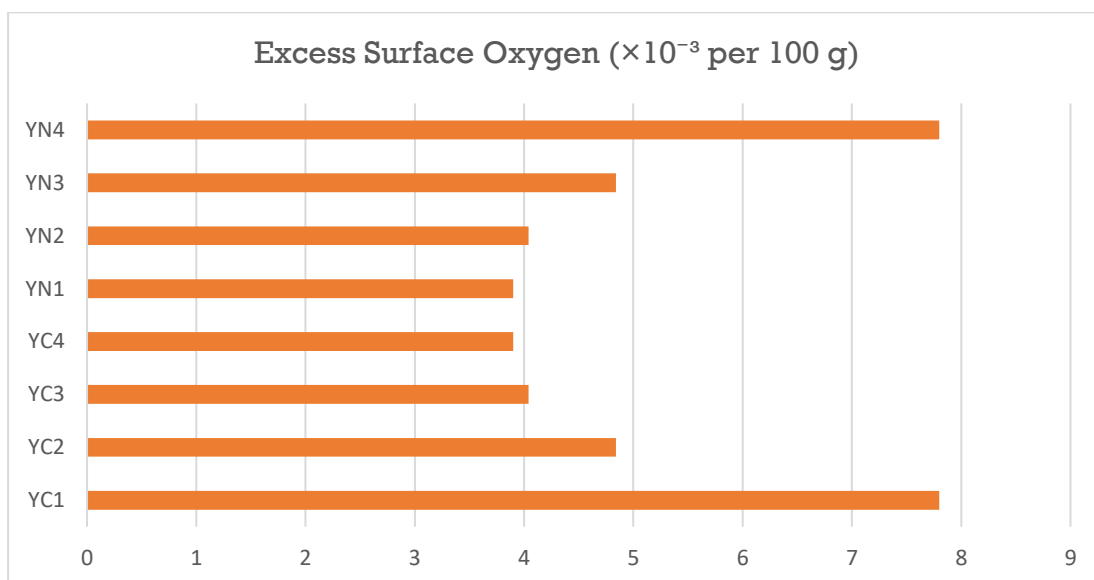
3.2 Oxygen Vacancies and Catalytic Activity

Oxygen vacancies play a significant role in catalytic processes because they enhance oxygen mobility and facilitate redox reactions.

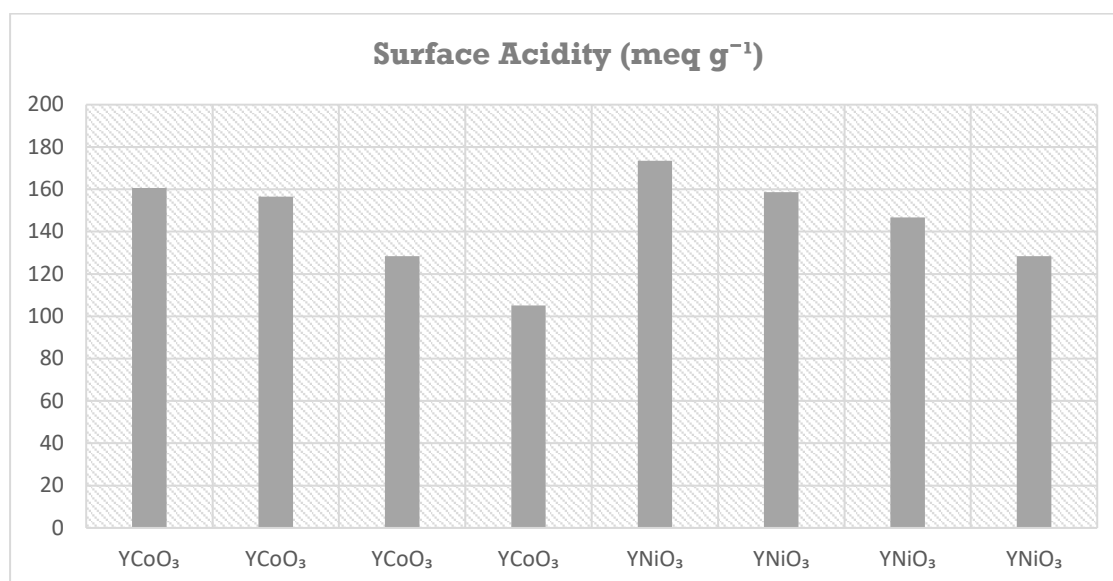
Experimental investigations on YCoO_3 and YNiO_3 perovskite systems further demonstrate the influence of calcination temperature on excess surface oxygen and acidity. A gradual decrease in ESO and surface acidity with increasing activation temperature indicates modification of surface catalytic sites and oxygen mobility.



(A)



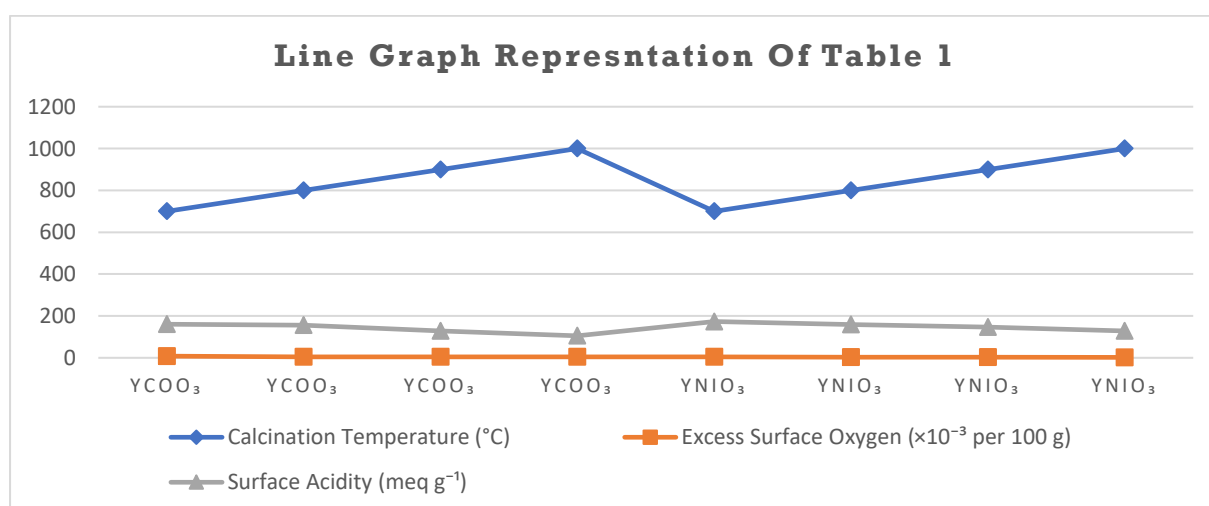
(B)



(C)

Graph 1. Surface Characteristics of YCoO₃ (YC1-C4) and YNiO₃ (YN1-) NPerovskite Catalysts at Different Calcination Temperatures.

- Increasing calcination temperature resulted in gradual reduction of excess surface oxygen and acidity.
- YNiO₃ samples exhibited comparatively higher acidity values, which may contribute to enhanced catalytic behavior.



Increasing oxygen vacancies can improve catalytic performance in reactions such as oxygen evolution and hydrogen evolution reactions (Liu et al., 2021).

The presence of oxygen vacancies also promotes adsorption of reactant molecules and accelerates surface reactions.



3.3 Synergistic Effect of Mixed B-site Cations

Mixed B-site perovskites such as $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$ show enhanced catalytic activity due to synergistic interactions between different transition metals.

Experimental studies have shown that $\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$ exhibits superior activity in CO and NO oxidation reactions due to improved oxygen vacancy formation and electron transfer properties.

Table 3: Catalytic Activity of Selected LnMO_3 Catalysts

Catalyst	Reaction	Conversion Efficiency
LaNiO_3	CO oxidation	High
LaCoO_3	CO oxidation	Moderate
LaMnO_3	ORR reaction	High
$\text{LaCo}_{0.8}\text{Mn}_{0.2}\text{O}_3$	CO/NO oxidation	Very high

4. Applications of LnMO_3 Catalysts

4.1 Environmental Catalysis

LnMO_3 perovskites are widely used in environmental catalysis, particularly for the removal of pollutants such as carbon monoxide, nitrogen oxides, and hydrocarbons.

Table 4: Environmental Applications of LnMO_3 Catalysts

Catalyst	Application
LaCoO_3	CO oxidation
LaFeO_3	Decomposition of organic pollutants
LaMnO_3	Oxygen reduction reaction
LaNiO_3	Benzene oxidation

Studies have demonstrated that LaMO_3 catalysts can effectively activate oxidants such as peroxymonosulfate for degradation of organic dyes and pollutants in water treatment processes.

4.2 Energy Conversion Applications

Perovskite catalysts are also used in:

- Solid oxide fuel cells
- Water splitting reactions
- Hydrogen production



Their high electronic conductivity and catalytic activity make them suitable for energy conversion technologies.

5. Mechanism of Catalysis in LnMO_3

The catalytic mechanism in perovskite oxides generally follows the **Mars–van Krevelen mechanism**, where lattice oxygen participates directly in oxidation reactions.

Steps of the mechanism

1. Adsorption of reactant molecules on catalyst surface
2. Reaction with lattice oxygen
3. Formation of oxygen vacancy
4. Reoxidation of catalyst by atmospheric oxygen

The ability of the catalyst to regenerate oxygen vacancies determines the efficiency of the catalytic cycle.

6. Results and Discussion

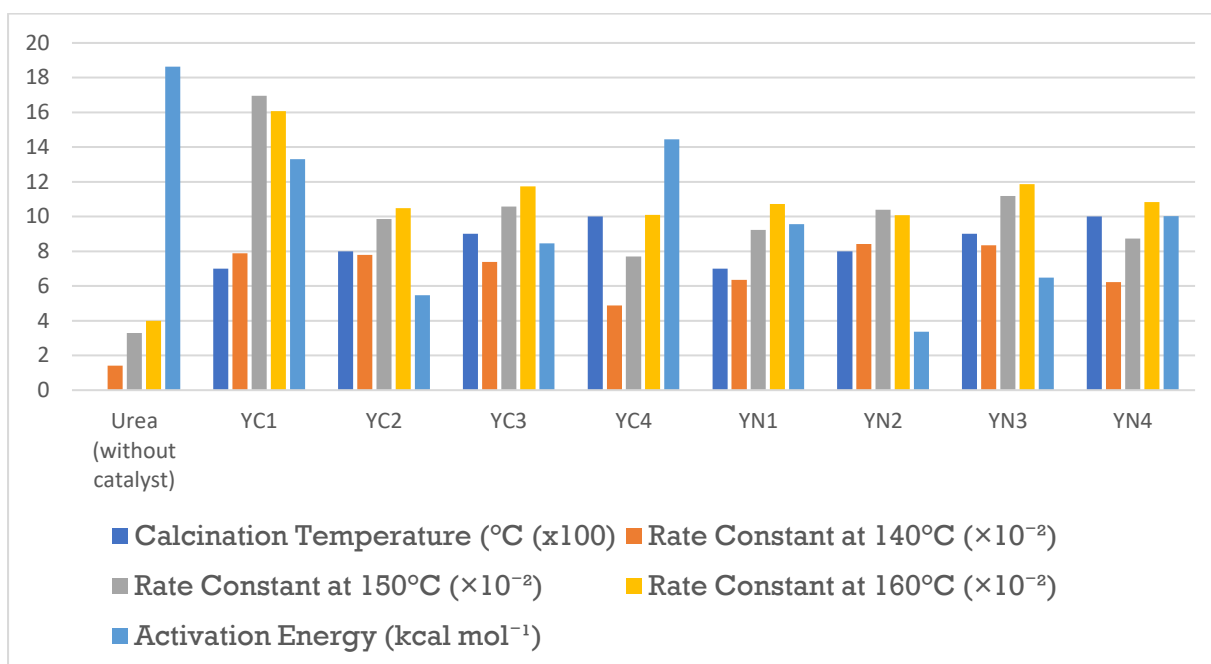
The catalytic properties of LnMO_3 oxides strongly depend on structural and electronic parameters.

Major factors influencing catalytic activity include:

- Type of transition metal at the B-site
- Oxygen vacancy concentration
- Surface area and particle size
- Mixed valence states of transition metals

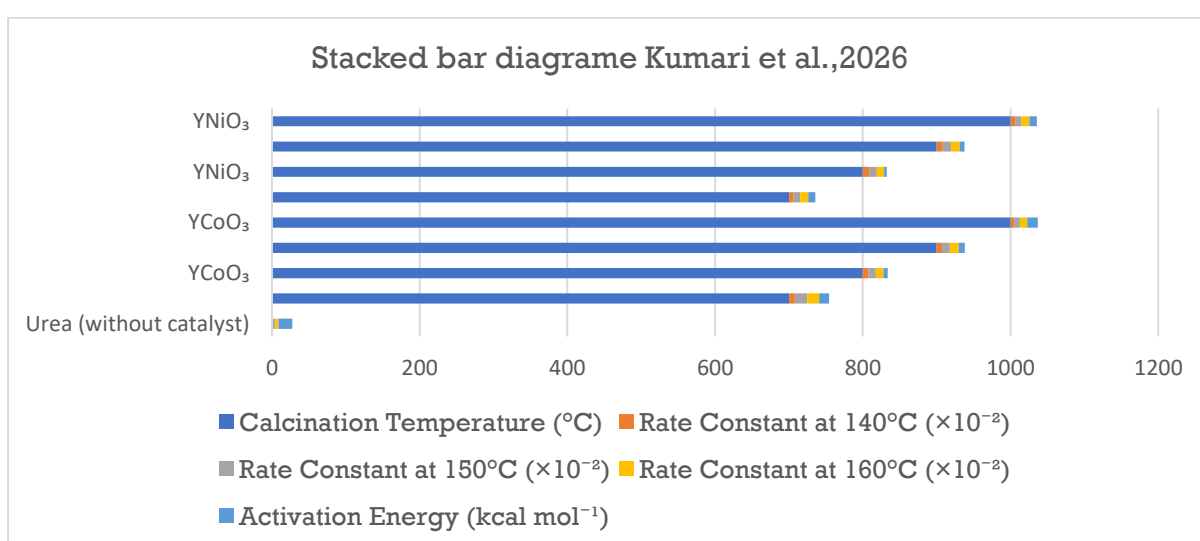
Experimental results from several studies indicate that **Co and Ni based perovskites generally exhibit higher catalytic activity than Fe and Mn-based systems** due to their higher redox flexibility.

Comparative kinetic studies on YCoO_3 (YC1-C4) and YNiO_3 (YN1-N4) catalysts during thermal -decomposition of urea reveal significant enhancement in catalytic efficiency relative to uncatalyzed systems. The catalytic activity was found to depend strongly on calcination temperature and transition metal composition.



Graph2 : Comparative Catalytic Activity of LnMO₃ Perovskites for Thermal Decomposition of Urea

- Both YCoO₃ and YNiO₃ perovskites significantly enhanced the thermal decomposition rate of urea compared to uncatalyzed reactions.
- YNiO₃ catalysts showed relatively lower activation energies, indicating superior catalytic efficiency.
- Catalytic performance was strongly influenced by calcination temperature and transition-metal composition.



Additionally, partial substitution of A-site ions with alkaline earth metals such as Sr can significantly increase catalytic activity by enhancing oxygen mobility.



7. Conclusion

Mixed oxides of transition metals with perovskite structures (LnMO_3) represent an important class of heterogeneous catalysts with remarkable catalytic properties. The structural flexibility of perovskites allows substitution at both A and B sites, enabling fine control over catalytic activity and selectivity. The catalytic behavior of these materials is primarily governed by the nature of the transition metal, oxygen vacancy concentration, and redox properties of the lattice.

LnMO_3 perovskites have shown great potential in environmental catalysis, energy conversion processes, and industrial oxidation reactions. Due to their low cost, high thermal stability, and tunable electronic properties, these materials are considered promising alternatives to noble metal catalysts in many applications. Future research should focus on nano-structured perovskites, surface engineering, and doping strategies to further enhance catalytic performance.

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