Comparative Analysis of Natural Perlite and Natural Mordenite as Catalysts

R.N. Shafieva[1*] , S.M. Abbasova[2],
M.F. Abbasov[1] · B.F. Shafiyeva[3]

[1]Ministry of Science and Education of Azerbaijan
Y.H. Mamedaliyev Institute of Petrochemical Processes, Baku, Azerbaijan
[2]Azerbaijan State University of Economy (UNEC), Baku, Azerbaijan
[3]Baku State University, Baku, Azerbaijan
`wafiyevar@gmail.com`

Abstract. The acetal formation reaction, which involves the condensation of an aldehyde with an alcohol, is a model acid-catalyzed reaction widely used in organic synthesis and fine chemistry. The efficiency of catalysts in this reaction depends on the surface acidity, accessibility of active sites, and resistance to deactivation. In this study, natural perlite and mordenite are investigated as promising, inexpensive, solid acidic catalysts for this reaction. One of the model reactions used to evaluate acid catalytic activity is the formation of cyclic acetals. In the reaction of benzaldehyde with glycerol in the presence of acid catalysts, 4-hydroxymethyl-2-phenyl-1,3-dioxolane, a cyclic acetal, is formed. The reaction is catalyzed by Lewis or Bronsted acids and is sensitive to the structure and accessibility of the catalyst surface active sites.

Keywords: Acetal, Natural Perlite, Natural mordenite, Benzaldehyde, Qlicerol,

1. Introduction

The acetalization reaction, representing the condensation of ketones and aldehydes with polyhydric alcohols, is one of the key acid-catalyzed processes in organic synthesis. It is widely used both in laboratory practice and industrial chemistry, where acetals serve as synthons, intermediates, protecting groups, and functional components in the pharmaceutical and polymer industries [1].

The efficiency of catalysts employed in this reaction directly depends on surface acidity, the accessibility of active sites, and resistance to deactivation [2,3]. Traditionally, homogeneous mineral acids have been used as catalysts for such reactions; however, their application is associated with corrosion problems, difficulties in product separation, and environmental risks. In this context, solid acid catalysts, such as natural aluminosilicates, represent a promising and sustainable alternative.

Particular attention is given to natural perlite and natural mordenite, which are abundant and inexpensive materials available in the Republic of Azerbaijan. Perlite is an amorphous volcanic glass that can be modified to enhance its catalytic activity. Mordenite, on the contrary, is a crystalline zeolite with a highly developed microporous

R. Rzayev et al. (eds.), *Proceedings of the International Conference on Current Problems in Engineering and Applied Sciences (ICCPEAS 2025)*, Advances in Engineering Research 299,
https://doi.org/10.2991/978-94-6239-668-5_24

structure and a high density of acid sites, making it naturally active in acid-catalyzed reactions.

This study aims to perform a comparative analysis of the catalytic activity of perlite and mordenite in the synthesis of cyclic aromatic acetals obtained from benzaldehyde and glycerol. The investigation focuses on the influence of structure and acidity on the efficiency of the reaction, as well as on assessing the potential of chemical modification of perlite and mordenite to enhance their catalytic performance.

2. Characterization of the Studied Aluminosilicates

Natural perlite (deposit: Gazakh, Republic of Azerbaijan) consists mainly of silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3). Its amorphous structure does not provide a high density of acid sites or sufficient surface accessibility, which leads to low catalytic activity in condensation reactions. The pore size of perlite corresponds to the mesoporous range (5–20 nm), and its specific surface area without modification is only 5–20 m^2/g, which can be increased up to 150 m^2/g after acid activation.

Natural mordenite (deposit: Jananab, Nakhchivan, Republic of Azerbaijan), in contrast, is a crystalline zeolite with a regular microporous framework. Its pores have an average diameter of approximately 0.7 nm, and the specific surface area reaches 250–400 m^2/g. The high density of acid sites (both Brønsted and Lewis types) ensures effective interaction of reagents with the catalyst and provides a high reaction rate. The key characteristics of these natural aluminosilicates are presented in Table 1.

Table 1. Physicochemical parameters of natural aluminosilicates

Parameter	Perlite (natural)	Mordenite (natural)
“Chemical composition, wt.%	SiO_2 – 72–75, Al_2O_3 – 12–14	SiO_2 – 65–70, Al_2O_3 – 10–12
Structure	Amorphous (volcanic glass))	Crystalline (zeolite framework)
Specific surface area, m^2/g	5–20 (up to 150 after activation	250–400
Pore volume, cm^3/g	0.1–0.2	0.3–0.5
Pore size	5–20 nm	~0.7 nm (narrow channels)
Surface acidity	Low	High (Bronsted and Lewis)

As seen from Table 1, natural perlite without modification exhibits limited catalytic properties, whereas mordenite initially possesses an optimal combination of acidity and microporosity, providing high catalytic activity.

To carry out the condensation reaction of benzaldehyde with glycerol, heterogeneous catalysts were prepared based on natural perlite and natural mordenite, modified with zirconium salts. The obtained catalyst samples were then tested for their activity in the condensation reaction of benzaldehyde with glycerol in the presence of an azeotrope-forming agent.

For the preparation of catalysts based on natural perlite and mordenite, rock samples were first crushed and sieved to obtain fractions of defined particle size, followed by stepwise dehydration. The dehydration was carried out initially at 120–150 °C for 4–6 hours, and then at 450–500 °C until a constant weight was achieved. The obtained perlite and mordenite samples were stored in an exsiccator and subsequently used for catalyst preparation.

Catalyst samples were prepared by impregnation of the dehydrated carrier with aqueous solutions of metal salts. The impregnation process was carried out under ambient conditions with continuous stirring for 24 hours. The materials were then dried at room temperature, followed by heating at 120 °C for 1.5–2 hours and calcination at 500 °C for 4–5 hours. The resulting catalysts were cooled and stored in an exsiccator until use. For each metal salt, 20 g of the carrier (natural perlite or mordenite) was impregnated with an aqueous solution of the corresponding metal salt (1–5 wt% relative to the carrier). After thermal treatment, the prepared catalysts were used in the condensation reaction of carbonyl compounds with diols.

The catalytic condensation reaction of benzaldehyde with glycerol was carried out at atmospheric pressure in a round-bottom flask equipped with a reflux condenser, Dean–Stark apparatus, mechanical stirrer, heater, and thermometer. The removal of water formed during the reaction (using an azeotrope-forming solvent) shifted the equilibrium toward acetal formation, increasing the product yield. The end of the reaction was determined by the cessation of water separation (based on the calculated amount).

3. Reaction mechanism of acetal formation

As a model process, the condensation of benzaldehyde with glycerol was investigated, leading to the formation of a cyclic acetal — 4-hydroxymethyl-2-phenyl-1,3-dioxolane.

The reaction proceeds via the following sequence of steps:

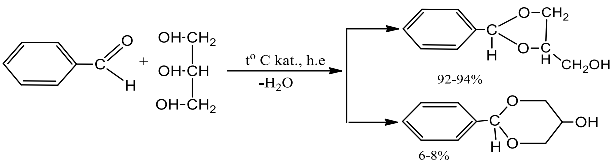
1. Protonation of the carbonyl group of benzaldehyde by the acidic site of the catalyst;
2. Nucleophilic attack of the hydroxyl group of the alcohol on the carbonyl carbon, forming a hemiacetal intermediate;
3. Cyclization of the hemiacetal with the elimination of water, yielding a stable cyclic acetal.

Investigation of the Condensation Reaction of Benzaldehyde with Glycerol in the Presence of Zirconium Sulfate–Modified Catalysts

In our previous studies on the catalytic condensation of benzaldehyde with ethylene and propylene diols, it was observed that the yield of the reaction products depends on the molar ratio of the reagents, the amount of catalyst, and the nature of the azeotrope-forming agent [6].

For the benzaldehyde–glycerol condensation reaction, the influence of several factors — such as reagent molar ratio, catalyst loading, solvent type, and reaction time — was systematically studied to determine optimal reaction conditions.

The catalytic condensation of benzaldehyde with glycerol proceeds according to the following general scheme, resulting in the formation of two cyclic acetal products.



The composition and structure of the synthesized aromatic acetals were determined using physicochemical analysis methods. It was found that the condensation products contain 92–94% of five-membered acetals and 6–8% of six-membered acetals. Although the formation of six-membered cyclic compounds is thermodynamically more favorable, the obtained product predominantly consists of five-membered acetals.

This observation can be explained by the fact that, at the initial stage of the reaction, after the attack of two hydroxyl groups within the pores of the heterogeneous catalyst surface, the approach of the third hydroxyl group becomes sterically hindered. As a result, the reaction mainly proceeds toward the formation of five-membered acetals.

Table 2. The results of the influence of various factors

Molar ratio of reagents I:II	Catalyst		Duration Hour	Yield of acetal in solvent, %		
	Q	%		Benzene	Toluene	Xylene
1:1	0,79	4	4	67,4	72,3	76,4
1:1,2	0,87	4	4	68,7	78,4	78,3
1:1,4	0,94	4	4	69,6	81,6	82,2
1:1,6	1,02	4	4	72,5	82,4	84,9
1:1,8	1,09	4	4	73,9	83,7	87,8
1:2	1.16	4	4	73,4	83,4	87,2
1:1,8	1,09	4	5	73,2	82,2	86,7
1:1,8	1,09	4	5	67,3	80,9	82,5

Analysis of the experiments presented in this table shows that, under identical conditions, increasing the molar ratio of benzaldehyde to glycerol from 1:1 to 1:2 leads to an increase in the acetal yield:from 67.4% to 73.9% when benzene is used as the solvent,from 72.3% to 83.7% in toluene,and from 76.4% to 87.8% in a xylene medium.

The condensation reactions generally reach completion within 4 hours, giving a high yield. Changing the reaction duration — either by shortening or extending it — does not lead to any improvement.

It was also found that a further increase in the molar ratio of reactants (1:2) causes a decrease in yield.

Considering all these factors, the optimal conditions for the catalytic condensation of benzaldehyde with glycerol were determined as follows: a molar ratio of 1:1.8, xylene as the solvent, a reaction time of 4 hours, and the use of zirconium sulfate–modified mordenite as the catalyst in an amount corresponding to 4 wt% of the reactants. Under these conditions, the yield of the aromatic acetal reaches 87.8%.

The acidic centers of the catalyst play a crucial role: Brønsted acid sites are responsible for the protonation and stabilization of intermediates, while Lewis acid sites activate the carbonyl group, enhancing nucleophilic addition. The accessibility of these sites within the pore structure of the catalyst affects both the reaction rate and product selectivity.

A comparison of the obtained data for the condensation of benzaldehyde with glycerol under identical conditions is presented in Table 3.

Table 3. Results of experiments evaluating the activity of natural and modified perlite and mordenite.

Catalyst	Percent conversion (%)	Yield of acetal, %	
Perlite (natural)	28	25	4
Perlite (H_2SO_4-modified)	52	48	3
Perlite ($ZnSO_4$)	68	65	3
Mordenite (natural)	82	79	2,5
Mordenite + $ZnSO_4$	89	91	2,5

4. Discussion of results

As can be seen, natural mordenite demonstrates the highest catalytic activity and selectivity, providing a faster conversion rate and a higher product yield. Its microporous structure and high density of acid sites facilitate efficient diffusion of reactants and activation of the carbonyl group.

Natural perlite, in its unmodified form, exhibits low activity, which is associated with limited acidity and restricted accessibility of active sites. However, after acid activation and impregnation with Zr^{2+} ions, its catalytic properties improve significantly, approaching those of mordenite. This makes modified perlite an economically attractive alternative for industrial processes.

The comparative analysis revealed that the efficiency of aluminosilicate catalysts directly depends on their acidity, porous structure, and availability of active sites. Microporous mordenite provides a high reaction rate and product selectivity, whereas perlite requires modification to achieve similar activity.

Furthermore, the removal of water is a key factor in increasing acetal yield. Efficient water removal from the reaction medium shifts the equilibrium toward product formation, enhancing conversion and selectivity.

A promising direction for further research on the obtained cyclic acetals is the development of hybrid catalysts that combine the low cost and availability of perlite with the high activity and selectivity of mordenite. Such an approach could lead to the creation of efficient, economical, and environmentally friendly reusable catalysts suitable for industrial applications.

5. Conclusion

The results of the condensation of benzaldehyde with glycerol show that, due to its microporous structure and high density of acid centers, mordenite exhibits superior activity and selectivity in the synthesis of aromatic acetals.

Natural perlite and mordenite in their unmodified forms possess relatively low catalytic activity, but after modification with zirconium salts, acid treatment, and ion impregnation, their catalytic properties improve considerably, leading to a higher acetal yield.

Modified perlite and mordenite can therefore serve as cost-effective catalysts, and the combination of their complementary properties opens new perspectives for developing hybrid catalytic systems for the condensation of carbonyl compounds with polyhydric alcohols.

References

1. Maltsev, A.P.: Tseolity v neftekhimii: struktura, svoistva, primenenie. Nauka, Moscow (2010).
2. Kresge, C.T., et al.: Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 359, 710–712 (1992).
3. Serrano, D.P., et al.: Acetalization of aldehydes over zeolites: acidity and molecular size effects. *Applied Catalysis A* 235(1–2), 79–89 (2002).
4. Il'inskii, G.A.: Kislotnye svoistva tseolitov i ikh primenenie v katalize. *Zhurnal Fizicheskoi Khimii* 78(6), 987–993 (2004).
5. Abbasov, M.F., Shafiyeva, R.N., Jafarova, A.A., Shafiyeva, B.F.: Synthesis of aromatic acetals in the presence of natural perlite. *Petroleum Processing and Petrochemistry* 26(3), 842–847 (2025).
6. Shafiyeva, R.N., Jafarova, A.A., Abbasov, M.F., Abbasova, S.M., Shafiyeva, B.F.: Təbii perlit iştirakında benzaldehidlə etilen və propilendiolların katalitik kondensləşmə reaksiyasının tədqiqi. In: *International Scientific Conference Dedicated to the "Year of Solidarity for a Green World"*, December 6, 2024, Baku, Azerbaijan, pp. 343–344.