

Reactivity and Regioselectivity in the Hydrogenative Ring-Opening of
Ethylcyclopropane and Methyloxirane over Preoxidized and Reduced
Transition Metal Catalysts

István Pálinkó, Ferenc Notheisz and Mihály Bartók
Department of Organic Chemistry, József Attila University,
Dóm tér 8., Szeged, H-6720 Hungary

Introduction

The results of a study concerning the activity and selectivity in the hydrogenative ring-opening of ethylcyclopropane (ECP) and methyloxirane (MOX) over preoxidized and reduced silica-supported Pt, Pd, Rh and Ni catalysts are reported in this paper. Much is known about the transition metal-catalyzed transformations of these molecules and they seem to be suitable for characterizing and comparing reduced and preoxidized metal surfaces. If the reaction conditions are mild, the predominant reaction is ring-opening, which is hydrogenative for ECP (giving only saturated hydrocarbons) (1), while MOX opens via isomerization as well (2). It is also known that cyclopropanes transform over metallic surfaces (3), while MOX is attached to the surface of the metal (4). Therefore, the ring-opening of ECP should be sensitive to a stable oxygen layer on the surface, while MOX should not.

In this work, the appropriate data-pairs are compared in order to describe the effects of preadsorbed oxygen.

Experimental

ECP was synthesized and purified in our laboratory through methods given in the literature (5), while MOX was purchased from Merck and was used without further purification.

The catalysts were made by impregnating a Cab-O-Sil (CS) support (BDH product) with chloride precursors or with $\text{Ni}(\text{NO}_3)_2$ (1). They were reduced after preparation (773 K, 16 hours, flowing hydrogen) and were kept in closed vials in a vacuum desiccator. The catalysts were of low dispersion (Table 1) and were characterized by H_2 and/or CO chemisorption, H_2 - O_2 titration and TEM. The chlorine contents of the catalysts were negligible, as revealed by X-ray fluorescence measurements. They were completely reduced, as verified by product composition (only saturated hydrocarbons were formed) and literature analogies (6).

catalyst	dispersion/%		particle size/nm	
	chemisorp.	TEM	chemisorp.	TEM
3.0% Pt/CS	11.8	11.5	8.6	8.8
3.0% Pd/CS	15.4	16.4	6.9	6.5
3.2% Rh/CS	27.0	24.4	3.9	4.3
3.0% Ni/CS	6.8	-	14.9	-

Table 1 Characteristic data on the catalysts

The reactions were run in a closed circulation reactor attached to a GC-integrator system allowing on-line monitoring of product distributions (for more details, see (7)).

Preoxidation was performed with dry air (5 minutes, temperature range 373-673 K).

The initial mixture contained 1.33 kPa of the hydrocarbon and 13.3 kPa of hydrogen. The reaction temperatures were 318 K, 373 K and 473 K for ECP, and 473 K for MOX. 5 to 25 mg of catalyst was used.

Results and discussion

The hydrogenative ring-opening of ECP gives exclusively saturated hydrocarbons as products (isopentane and n-pentane) (1). There is no fragmentation over Pt, Pd or Rh. Cracking products can be seen over Ni/CS, but the ring-opening products predominate here as well (1/c). The ring opens overwhelmingly in the sterically less hindered direction, but 1,2 C-C bond rupture always occurs too. For MOX, the situation is somewhat more complicated: isomerization (to propionaldehyde and acetone) always accompanies hydrogenation (to n-propanol and isopropanol), and minor amounts of cracking products are also formed on each catalyst (2). Here, O-C bonds are cleaved, predominantly the sterically less hindered ones, over Pt, Pd and Rh. The regioselectivity is the opposite over Ni/CS.

Preoxidation of the catalyst does not lead to new reaction pathways. There are no new products for any of the hydrocarbons. However, oxidation affects the activity and the selectivity of the reactions of the two compounds in fundamentally different ways. For MOX, preoxidation does not influence either the activity or the regioselectivity of the reaction (except for the activity over Ni/CS) (Tables 2 and 3), proving that adsorption starts at the oxygen atom, i.e. MOX itself oxidizes the catalyst and the

reaction proceeds over a partially oxidized surface even in the absence of preadsorbed oxygen.

temperature of oxidation/K ^a	catalysts			
	Pt/CS ^b	Pd/CS ^c	Rh/CS ^c	Ni/CS ^c
473	-	1.0	1.0	1/ 1.5
523	1.0	1.2	1.1	1/ 4.0
573	1.0	1.0	1.0	1/ 8.9
623	1.1	1.1	0.9	1/ 9.9
673	-	1.1	1.1	1/11.0

Table 2 The relative activity (r_{ox}/r) in the ring-opening of MOX at different preoxidation temperatures

temperature of oxidation/K ^a	catalysts			
	Pt/CS ^b	Pd/CS ^c	Rh/CS ^c	Ni/CS ^c
473	-	1.1	0.8	1.2
523	1.1	0.9	0.9	0.9
573	1.0	0.9	1.0	0.8
623	1.1	1.1	0.9	1.2
673	-	1.1	1.0	1.1

a preoxidation with air, 5 min

b 20.0 mg catalyst, reaction temperature 473 K, H₂ pressure 13.3 kPa

c 12.5 mg catalyst, reaction temperature 473 K, H₂ pressure 13.3 kPa

Table 3 The relative selectivity (S/S_{ox}) in the ring-opening of MOX at different preoxidation temperatures (S=2,3 bond scission/1,2 bond scission)

The situation is more complex with ECP. There is no change in any of the parameters over Pt/CS, but the activity increases (relative to that of the untreated catalyst) over Pd/CS, and decreases for Rh/CS and Ni/CS (Table 4). However, the regioselectivity is not affected over any of the catalysts (Table 5).

temperature of oxidation/K ^a	catalysts			
	Pt/CS ^b	Pd/CS ^c	Rh/CS ^d	Ni/CS ^e
373	1.3	1.7	-	-
473	1.3	3.0	1/2.0	1/ 1.9
523	1.3	3.1	1/4.2	1/ 9.8
573	1.3	3.1	1/7.5	1/10.4
623	-	3.6	1/8.5	1/ 9.4
673	-	3.7	-	1/ 9.1

Table 4 The relative activity (r_{ox}/r) in the ring-opening of ECP at different preoxidation temperatures

temperature of oxidation/k ^a	catalysts			
	Pt/CS ^b	Pd/CS ^c	Rh/CS ^d	Ni/CS ^e
373	1.0	1.6	-	-
473	1.0	2.0	1.2	0.9
523	1.0	1.9	1.1	1.0
573	1.0	1.8	1.0	1.0
623	-	1.8	1.0	0.9
673	-	1.7	-	1.0

a preoxidation with air, 5 min

b 5.0 mg catalyst, reaction temperature 318 K, H₂ pressure 13.3 kPa

c 12.5 mg catalyst, reaction temperature 373 K, H₂ pressure 13.3 kPa

d 12.5 mg catalyst, reaction temperature 318 K, H₂ pressure 13.3 kPa

e 25.0 mg catalyst, reaction temperature 473 K, H₂ pressure 13.3 kPa

Table 5 The relative selectivity (S/S_{ox}) in the ring-opening of ECP at different preoxidation temperatures (S=2,3 bond scission/1,2 bond scission)

However, the regioselectivity shifts towards 1,2 C-C bond scission when the hydrogen partial pressure is lower than 13.3 kPa (Table 6).

temperature of oxidation/K	H ₂ pressure/kPa					
	1.3		6.7		13.3	
	r/r _{ox}	S/S _{ox}	r/r _{ox}	S/S _{ox}	r/r _{ox}	S/S _{ox}
473	1.5	1.3	1.4	1.0	1.9	0.9
523	3.2	2.2	8.6	1.2	9.8	1.0
573	4.8	2.1	20.7	1.9	10.4	1.0
623	-	-	-	-	9.4	0.9
673	2.3	1.9	16.1	1.4	9.1	1.0

Table 6 Effects of the H₂ pressure on the activity and selectivity in the ring-opening of ECP over a preoxidized Ni/CS catalyst (reaction temperature 473 K)

The data in the Tables clearly show the effects of preoxidation on the ring-opening reactions:

MOX

- Neither activity nor regioselectivity changes are observed over Pt/CS, Pd/CS or Rh/CS;
- the activity decreases over Ni/CS, but the selectivity does not change.

ECP

- Neither activity nor regioselectivity changes are observed over Pt/CS;

- the activity increases appreciably over Pd/CS, and the regioselectivity shifts towards the scission of the sterically more hindered C-C bond (but 2,3 bond rupture still predominates);
- the activity decreases over Rh/CS, but there is no change in the regioselectivity;
- the same is true for Ni/CS, but upon decrease of the hydrogen pressure the regioselectivity shifts towards 1,2 C-C bond scission (though 2,3 bond rupture still predominates),

The following explanations can be offered for consideration:

- (1) the stability of the oxide layer over Pt/CS is low, and hydrogen in the reaction mixture is able to remove it upon first contact;
- (2) high-temperature oxidation removes β -hydride from Pd/CS, and therefore the initial activity increases and the regioselectivity changes as well (for a more detailed discussion, see (1/b));
- (3) a relatively stable chemisorbed oxygen layer decreases the activity of Rh/CS, but there is no oxide formation, i.e. the electronic structure of the uncovered metal surface does not change, as shown by the unchanged regioselectivity;
- (4) the oxidation of Ni/CS results in surface and bulk oxide formation, as shown by a dramatic activity decrease and a regioselectivity shift; the colour of the catalyst also changes from black to light-green upon oxidation.

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