Activity and regioselectivity in the ring-opening reaction of methyloxirane at metal–metal oxide interfaces

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Abstract

Hydrogenative ring-opening reactions of methyloxirane (MOX) were performed over reduced and preoxidized silica-supported Pt, Pd, Rh, Ni and Cu catalysts in order to study reactions at metal–metal oxide interfaces. A comparison of the activity, as well as ring-opening selectivity data over the reduced and preoxidized surfaces, revealed that MOX adsorbed through the ring oxygen and itself oxidized the metal surfaces. This means that the active sites for its catalytic transformations are ionic species formed in situ at the metal–metal oxide interface. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The transition metal-catalyzed transformations of ring systems of various sizes still belong to important topics of research. Earlier, the ring-opening reactions were mainly studied from a mechanistic point of view (for a review, see Ref. [1]). Recently, since much molecular level information has been gathered about these reactions, they are mainly used as test reactions. Of course, research was focused on the more accessible hydrocarbon rings, especially on derivatives of cyclopropane [2–6] and cyclopentane [7–9] and quite recently (although their synthe-

sis is difficult) on alkyl-substituted cyclobutanes [10–13].

Just a handful of recent papers has been concerned with the metal-catalyzed reactions of ring systems with heteroatom(s) (for a review and the papers, see Refs. [14,15]). It is regrettable, since ring compounds with, e.g., an oxygen atom (or atoms) offers the possibility of studying the reactivity and selectivity of in situ formed metal–metal oxide interfaces. This kind of research may even be more valuable if results can be compared with those of hydrocarbon ring systems of the same size. Interfaces of various types (e.g., metal–carbonaceous deposit, metal–support, metal and its oxide) often exert peculiar effects on the activity and/or selectivity of metal-catalyzed transformations. However, the proportion of reactions occurring at

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these sites is difficult to assess and they can rarely be studied separately, since transformations proceeding over the metal surface may cover these effects. A method for studying reactions at the interface of metal and its oxide may be the increase of the relative quantity of the interface by preoxidizing the supported metal and comparing the change in activity and selectivity to the untreated supported metal. In this work, results of such comparison are described using silica-supported Pt, Pd, Rh, Ni and Cu catalysts and the hydrogenative ring-opening of methyloxirane (MOX).

2. Experimental

2.1. Materials

The catalyst support was a Cab-O-Sil M5 silica from BDH (BET surface area: 241.6 m^2 g^{-1}). The 3.0% Pt/SiO$_2$, 3.0% Pd/SiO$_2$, 3.2% Rh/SiO$_2$ and 3.0% Ni/SiO$_2$ catalysts were prepared by impregnation using the aqueous solutions of the appropriate metal salts (chlorides in most cases, except for Ni/SiO$_2$ where the nitrate was applied). The air-dried catalysts were reduced under hydrogen flow at 773 K for 16 h. The percentage of exposed metal atoms was determined by hydrogen chemisorption (Pt/SiO$_2$, Rh/SiO$_2$, Ni/SiO$_2$) or CO chemisorption (Pd/SiO$_2$) at 298 K in a flow system. The catalysts were of low dispersion: Pt/SiO$_2$ —11.8%, Pd/SiO$_2$—15.4%, Rh/SiO$_2$— 27.0%, Ni/SiO$_2$—6.8% (in calculations, 1:1 adsorption stoichiometry was assumed). The 6.8% Cu/SiO$_2$ catalyst was made by precipitating copper–hydroxide–carbonate on the surface of the support. After preparation, it was reduced in hydrogen flow (473, 523 K, and 573 K with 1-h hold at each temperature). The dispersion (number of surface Cu atoms/number of Cu atoms) was determined by N$_2$O titration at 373 K in a flow system. It was 12.3%. The amount of Cu(I) ions remained on the surface after the reduction was determined by temperature pro-

grammed reduction (TPR) and was found to be 10.3%.

Methyloxirane was a commercial product (Merck), ethylcyclopropane (ECP) was synthesized in our laboratory. Hydrogen was produced by a Matheson hydrogen generator.

2.2. Reactor and methods

Reactions were studied in a closed recirculation reactor. The initial mixture contained 1.33 kPa of MOX (or ECP) and 13.3 kPa of hydrogen. Reaction temperatures were 473 K for MOX (318 K for ECP). An amount of 5 to 20 mg of catalyst was used. Preoxidation of the catalyst was performed at various temperatures in the 473–673 K range (usually with 50° increments) under flowing dry air. Product accumulation was followed by gas chromatography. From the product accumulation vs. time data, initial activity values (in turnover frequencies) and initial ring-opening selectivities were calculated and compared over the reduced and preoxidized catalysts.

3. Results and discussion

Methyloxirane underwent isomerization and hydrogenation upon ring-opening in hydrogen atmosphere over the reduced catalysts. Isomerization products were acetone and propionaldehyde (occasionally allyl alcohol was also formed), hydrogenation produced *n*-propanol and 2-propanol (Scheme 1).
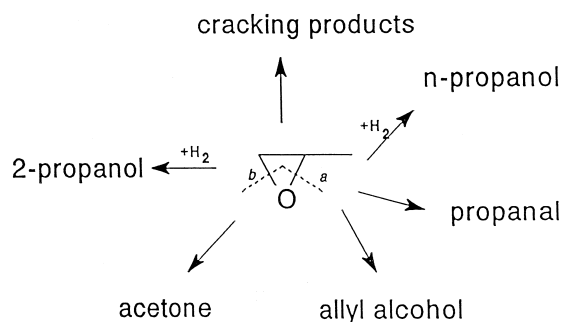
Scheme 1. Transformation routes of methyloxirane upon hydrogenative ring-opening.

Table 1

Relative activity data (r_{ox}/r) in the hydrogenative ring-opening of MOX at various preoxidation temperatures

Temperature of preoxidation (K)	Catalysts				
	Pt/SiO_2^b	Pd/SiO_2^c	Rh/SiO_2^c	Ni/SiO_2^c	Cu/SiO_2^c
473	–	1.0	1.0	1/1.5	1/1.8
523	1.0	1.2	1.1	1/4.0	1/1.8
573	1.0	1.0	1.0	1/8.9	1/4.6
623	1.1	1.1	0.9	1/9.9	–
673	–	1.1	1.1	1/11.0	–

[a] Preoxidation with dry air, 5 min.
[b] 20.0 mg catalyst, reaction temperature 473 K, H_2 pressure 13.3 kPa.
[c] 12.5 mg catalyst, reaction temperature 473 K, H_2 pressure 13.3 kPa.

Following the ratio of products derived from the rupture of the sterically more hindered C–O bond and that of the less hindered one, the changes in activity can be good measures of catalyst transformations occurring upon oxidation (Tables 1 and 2).

After collecting and calculating data obtained at (in most cases) five preoxidation temperatures, it was clear that preoxidation did not change the catalytic surface necessary for the ring-opening over Pt/SiO_2, Pd/SiO_2, Rh/SiO_2. This means that neither the activity nor the selectivity has changed. These results indicate that the MOX molecule itself oxidizes the surface of these catalysts, i.e., adsorption starts at the oxygen atom in the ring and this self-oxidized ionic surface serves as the catalyst. It also contains metal atoms, since MOX does not fully cover the surface and hydrogen is also present as co-reactant and as in situ reducing agent. Preoxidation does not change the picture, but the surface favourable for the adsorption of

the molecule is ready-made and the hydrogen co-reactant reduces part of the surface upon contact and hydrogen adsorbs and dissociates over the reduced metal atoms.

As far as ring-opening activities are concerned, Ni/SiO_2 showed severe deactivation upon the increase in preoxidation temperature. This is clear indication that significant changes occurred. Indeed, even visual inspection could detect the change, that is, the colour of the catalysts turned from black (the colour of the reduced catalysts) to greenish. Most probably, in-depth oxidation took place and Ni ions were formed. Under the reaction conditions, hydrogen present in the reacting mixture could not rereduce (it is known that the reduction of Ni(II) ions is not a facile process) large portion of the ions. Since metal atoms are necessary for the dissociation of hydrogen and hydrogen atoms are prerequisites for the ring-opening to proceed, the rate of the reaction decreased. Regioselectivity of the ring-opening did not change,

Table 2

Relative selectivity data (S/S_{ox}) in the hydrogenative ring-opening of MOX at various preoxidation temperatures ($S = 1,3$ bond scission/1,2 bond scission $= b/a$)

Temperature of preoxidation (K)	Catalysts				
	Pt/SiO_2^b	Pd/SiO_2^c	Rh/SiO_2^c	Ni/SiO_2^c	Cu/SiO_2^c
473	–	1.1	0.8	1.2	1.3
523	1.1	0.9	0.9	0.9	1.3
573	1.0	0.9	1.0	0.8	1.9
623	1.1	1.1	0.9	1.2	–
673	–	1.1	1.0	1.1	–

[a] Preoxidation with dry air, 5 min.
[b] 20.0 mg catalyst, reaction temperature 473 K, H_2 pressure 13.3 kPa.
[c] 12.5 mg catalyst, reaction temperature 473 K, H_2 pressure 13.3 kPa.

however. This is a clear indication that the mechanism, i.e., the active site composition, did not change.

The Cu/SiO_2 catalyst behaved somewhat differently. Preoxidation also decreased the ring-opening rate; however, the regioselectivity was shifted towards the scission of the sterically more hindered C–O bond. The explanation for the activity decrease may be similar to that of the Ni/SiO_2, i.e., in-depth oxidation occurred and rereduction of Cu(II) ions is at least as difficult as that of the Ni(II) ions. The suggestion is that the selectivity shift over the oxidized catalyst is due to the presence of Cu(II) not available over the reduced catalyst. Here, as it is pointed out in Section 2, Cu(I) ions remain even after reduction. The higher proportion of ionic species and their higher acidity may rationalize the observed selectivity shift.

Preoxidation can be disadvantageous on other ring-opening reactions, however. For comparison, similar treatments were applied using the hydrogenative ring-opening of ECP as probe reaction. This molecule undergoes exclusive hydrogenation, giving pentane and isopentane over Pt/SiO_2, Pd/SiO_2 and Rh/SiO_2. Some fragmentations take place over Ni/SiO_2; however, hydrogenative ring-opening still predominates. The ring opens in the sterically less hindered direction, but 1,2 C–C bond rupture always occurs. In these transformations, severe deactivation and regioselectivity shifts were observed.

4. Conclusion

Through comparing activities and ring-opening selectivities in the hydrogenative ring-opening of MOX over reduced and preoxidized supported transition metal catalysts, it was found that the presence of a metal–metal oxide interface is necessary for the reaction to proceed. This interface is produced in situ over the reduced catalysts by the preferential adsorption of MOX through its ring oxygen. Preoxidation makes the oxidized ionic surface; however, now, a part of metal ions produced must be rereduced by hydrogen to obtain a reasonable ring-opening rate.

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