

Metathesis of C₅–C₈ Terminal Olefins on Re₂O₇/Al₂O₃ Catalysts

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Abstract Primary products of the interaction of terminal olefins C_5 - C_8 with Re_2O_7/Al_2O_3 catalysts are established. The rupture of the C=C bond of the olefin occurs with formation of a carbene localized at a rhenium ion, with the



alkylidene fragment in the produced carbene being the CH_2 =group of the terminal alkene molecule. Thus M=CH₂ species and lower normal α -olefins are formed.

Graphical Abstract

Primary products formed from terminal Olefins C_5 - C_8 on the activated Re_2O_7/Al_2O_3 catalysts are established. The rupture of the starting alkene at the first instant leads to the formation of M=CH₂ species and lower normal α -olefins.

Keywords Metathesis $\cdot \alpha$ -olefin C₅–C₈ \cdot Re-containing catalyst \cdot Aluminum oxide \cdot Olefin metathesis active site \cdot Carbene

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1 Introduction

Quite intensive studies of the theoretical and experimental aspects of olefin metathesis became the basis of the wide application of this reaction in organic synthesis and petrochemistry [1, 2].

Homogeneous or heterogenized metal complexes (Schrock or Grubbs systems) are known as active metathesis catalysts [3]. Heterogeneous catalysts are also know in the

art, including diverse Mo-, W- and Re-supported systems based on different oxide carriers, with alumina being the most abundant one [4]. Rhenium-containing heterogeneous catalysts are typically most active among the heterogeneous analogs. [5] The formation of active metathesis sites occurs during the interaction of the olefinic substrate molecules with the preactivated catalyst. It is generally supposed that carbene Re complexes are the result of such an interaction [5, 6]. However numerous spectroscopic studies, including IR spectroscopy [2, 7–11], Raman spectroscopy [12–14], ESR [15–17], Moessbauer spectroscopy [18, 19], XPS [20– 24], and XAFS [11, 25, 26] have not provided convincing experimental support for this concept so far: the assumed active reaction intermediates have not been detected using a handful of the sensitive and informative methods. A few publications are known where the authors tried to reveal the nature and to postulate the structure of the metathesis reactive species by analyzing the very initial products formed at the first contact of the alkene with the catalyst [27, 28]. Nevertheless, the results obtained did not bring an unequivocal answer either. Some authors consider 1-butene formed during the metathesis of propene as a product of isomerization of 2-butene [27]. However, such a migration of the double bond is not quite agreeable with thermodynamics of the system. The peculiar features of the conditions and procedures used by different authors in studying the reaction of alkene metathesis (olefin/Re ratio, addition of certain organometallic activators, types of the reactors used in the experiments) make the adequate comparison of the literature data difficult.

It was assumed that ethylene is not capable of activating the catalyst in the metathesis reaction [2, 28], but other authors reported on the formation of small amounts of propene and 2-butene when ethylene was supplied to the rhenium catalyst [29]. Only two metathesis reaction products were found upon the interaction of 1-heptene or 1-octenewith CsNO₃-Re₂O₇-Al₂O₃ in a plug-flow reactor: dodecene-6 or tetradecene-7, respectively, and ethylene [30]. However in the case of 1-hexene, some amounts of 2-heptene and 4-nonene were detected in the metathesis products in addition to decene-5. C₅, C₇, C₈, C₉, and C₁₁ olefins were identified in metathesis of 1-hexene, beside the main product, i.e. 5-decene, but the structure of these olefins and their origin were not revealed [31]. The NH₄ ReO₄-Al₂O₃ catalyst calcined at 550 °C and γ -irradiated in a reducing atmosphere of CH4 or CO demonstrates a rather high activity. The 1-hexene conversion is close to 60 %, however, the authors failed to identify the presumably active π - or Reⁿ⁺=CH₂ complexes. The conclusion drawn by the authors is quite heuristic: the interaction of methane with the surface species leads to the formation of a Re-CH3 moiety and further possible genesis of Re=CH₂ by proton transfer or elimination of a water molecule.

It should be noted that a number of interesting publications appeared just recently on the subject. Analysis of the literature data on terminal alkene metathesis [32-37] reveals the general experimental peculiarities in the tests aimed at establishing the composition and structure of the products of interaction of a C_n terminal alkene with the forming active sites:

- At high initial olefin:Re ratios, the reaction mixture contains, as a rule, only two main products—ethylene and the expected C_{2n-2} metathesis product;
- Other alkenes qualified as side products are observed at reduced alkene:Re ratios.

The goal of the present study is to find new data about the products of the primary interaction of terminal C_5-C_8 alkenes with the sites located at the activated surface of the Re₂O₇-Al₂O₃ catalyst, with these products being formed at the very initial instants of the contact of the terminal alkenes with the active sites at different alkene:Re molar ratios.

2 Experimental

2.1 Catalysts and Materials

Re/alumina catalysts ([Re] = 3, 6, or 9 wt.%) were prepared by incipient wetness impregnation of y-Al₂O₃ (Ryazan refinery, specific surface area 196 m^2/g , size of the particles 0.3-0.6 mm) with an aqueous solution of NH₄ ReO₄ (Aldrich), the impregnated samples were kept for 2 h at 20 °C and dried 2 h at 150 °C. Before the catalytic tests, the catalysts were calcined in a flow of dry air for 1.5 h at 520-550 °C and then cooled to room temperature in an Ar flow. The catalytic tests were performed both in a plugflow reactor and in a batch reactor under stirring. The reactor was loaded with 0.14-0.7 g of a catalyst both in the flow and batch conditions. The reactions of 1-pentene, 1-hexene, 1-heptene, and 1-octene metathesis was studied at room temperature using *n*-heptane as a diluent, except for the case of 1-heptene metathesis when n-octane was used as a solvent. All the hydrocarbons were preliminarily purified by distillation in an Ar flow over metallic Na and were kept over NaA molecular sieve calcined at 500 °C in argon. The purity of alkenes was better than 99 %. The molar ratio alkene: Re was varied from 0.2 to 100.

Deuterated hexene-1,1-D₂-1-hexene was prepared using the reaction:

 $CH_{3}(CH_{2})_{3}CH_{2}COOCH_{3} \xrightarrow{\text{LiAlD}_{4}} CH_{3}(CH_{2})_{3}CH_{2}CD_{2}OD$ $CH_{3}(CH_{2})_{3}CH_{2}CD_{2}OD$ $+ (CH_{3}CO)_{2}O \rightarrow CH_{3}(CH_{2})_{3}CH_{2}CD_{2}OOCCH_{3}$

 $CH_3(CH_2)_3CH_2CD_2OOCCH_3 \xrightarrow{\Delta} CH_3(CH_2)_3CH = CD_2$

2.2 Metathesis in a Batch Reactor

A catalyst sample (0.14 g) was transferred in a flow of argon into the reactor (a two-neck flask), and 1 ml of an alkene in 2 ml of *n*-heptane (*n*-octane) was added. The duration of the catalytic experiment at 20 °C and 1 atm was 1 h.

2.3 Metathesis in a Flow Reactor

A catalyst loading (0.7 g) was transferred in a flow of argon into the quartz tubular and a flow of argon was bubbled through a saturator with an alkene at 20 °C with the Ar flow rate of 30 ml/min. The duration of the catalytic experiment at 20 °C and 1 atm was 3 h. In studying the dependence on the space velocity (or reverse conventional contact time), we varied the weight hourly space velocity from 0.75 h⁻¹ (conventional contact time 80 min) to 60 h⁻¹ (1 min) while varying the catalyst loading.

2.4 Metathesis of 1,1-D₂-1-Hexene

The Re₂O₇/Al₂O₃ catalyst (9 wt.% Re) prepared as described above was calcined at 520 °C for 2 h, then the sample was transferred in a flow of argon into the reactor (a two-neck flask), and 1 ml of 1,1-D₂-1-hexene was added with 2 ml of *n*-heptane. The duration of the catalytic experiment was 1 h. The conversion of the alkene was 3 %.

2.5 Analysis of Products

Analysis of the gas reaction products was carried out using an LKhM-8MD chromatograph with a thermal conductivity detector at 120-150 °C with a packed column $(1.5 \text{ m} \times 3 \text{ mm})$ filled with Separon. Liquid products were analyzed using a packed column (3 m \times 3 mm) with SE-30. Helium served the carrier gas. *n*-Hexane was used as an internal standard for quantitative analyses. Additionally identification of all the reaction products was performed using a MS-GC method using a FOCUS DSQ II chromatomass-spectrometer with a TR-5 ms capillary column (50 m). For deuterated products the analysis was done with mass-spectrometry. In performing the metathesis reaction, the analysis of the gas and liquid products was performed at the moment of the initial contact of the 1-alkene used as a substrate with the catalyst (0.25-1 min) and at the steady state of the process (with the time on stream or residence time of up to 2 h). The composition of the reaction products formed was studied most carefully in the case of 1-hexene metathesis.

3 Results and Discussion

The reaction of metathesis of terminal alkenes proceeds according to the following scheme (Eq. 1)

$$2CH_3(CH_2)nCH = CH_2 \rightarrow CH_3(CH_2)nCH$$
$$= CH(CH_2)nCH_3 + CH_2 = CH_2(n=2-5)$$
(1)

Since Al_2O_3 or Al_2O_3 SiO₂ are used most often as the carriers for the heterogeneous metathesis catalysts, we studied first the possibility of the conversion of 1-hexene on these supports under the conditions of the metathesis reaction. It follows from the data of Table 1 that γ -Al₂O₃ demonstrates a substantially different behavior as compared to Al₂O₃SiO₂. These data show that silica-alumina, obviously due to the presence of rather strong acid sites (revealed in previous studies by diffuse-reflectance FT-IR spectroscopy using CO and acetonitrile as probe molecules [38]), catalyzes predominantly the reactions of isomerization, di- and trimerization of the starting alkene. Therefore, we have chosen γ -Al₂O₃ as the carrier for the further studies of the metathesis reaction.

The products of 1-hexene interaction with the activated Re/Al₂O₃ catalyst include two groups of alkenes: terminal alkenes (ethylene, propene, 1-butene and 1-pentene) and internal alkenes (2-heptene, 3-octene, 4-nonene and 5-decene). Independently on the conditions of the process (flow or batch-wise), on the concentration of rhenium and on the temperature of the catalyst, the main metathesis products (5-decene and ethylene) predominated, with the selectivity to this couple increasing with increasing the starting alkene: Re molar ratio. The formation of terminal olefins (except for ethylene) during 1-hexene metathesis was surprising, since it was known from the previous art that terminal olefins can be produced in the metathesis process only via the interaction (co-metathesis) of alkenes with the internal double bond with ethylene (ethenolysis) or with another 1-alkene. According to the notions presently accepted in the literature [2, 39] Re-carbene complexes are considered as active reaction intermediates in metathesis, and the exchange of alkylidene fragments as a result of the C=C bond rupture [40] was experimentally proved. Thus, the qualitative product composition obtained allows us to believe that the initial contact of the reacting 1-alkene with the Re₂O₇/Al₂O₃ catalyst results in the

Table 1 Conversion of 1-hexene on γ -Al₂O₃ and 24.5 %Al₂O₃/SiO₂ at 200 °C (olefin/catalyst ratio 5, duration 1 h, batch experiment)

Support	Composition of the products (wt.%)							
	2-Hexene	3-Hexene	Dimers	Trimers				
Al ₂ O ₃								
Al ₂ O ₃ ·SiO ₂	14.8	10.3	2.7	1.8				

Time (min)	Composition of gas products (wt.%)		Composition of liquid products (wt.%) ^a						
	Ethylene	Propene	Propene	1-Butene	1-Pentene	3-Octene	4-Nonene	5-Decene	
0.75				Traces	0.5				
1.75			Traces	0.3	0.8		0.3	1.4	
3	Traces		0.5	1.3	2.1	0.7	3.1	3.9	
10	56	44	0.7	2.1	3.7	1.2	4.5	28.7	
30	78	22	0.05	0.8	2.5	5.1	7.3	45.2	

Table 2 Metathesis of 1-hexene in the batch reactor (9 wt.% Re/Al₂O₃, alkene:Re = 1:5 (mol.), T = 200 °C, solvent—*n*-heptane)

^a 2-Heptene formed in 1-hexene metathesis (Table 2) was not identified in this run because of the close retention time with *n*-heptane

generation of the active sites by direct C=C bond rupture with the formation of a carbene localized on a rhenium ion. The role of the alkylidene fragment in the carbene active species is played by the smaller (by molecular weight) fragment of the starting 1-hexene molecule, which is confirmed by the presence of 1-pentene in the reaction products. This is also confirmed by the experiments performed under batch conditions: only 1-pentene was found in the liquid phase during the very initial period (45 s) of the process of 1-hexene conversion (Table 2). At this very instant, no products were detected in the gas phase.

Other products, which are formed and become detectable in the liquid products together with 1-pentene with the further development of the process in time, include propene, 1-butene, 3-octene, 4-nonene, and the main product expected in the metathesis of 1-hexene, namely, 5-decene.

It should be noted that the rupture of the olefin molecule at the initial moment of the reaction on the activated Re/ alumina catalyst with the formation of Re=CH₂ and CH₂=CH(CH₂)₂CH₃, as well as other α -alkenes was not unequivocally experimentally observed so far.

The ways of the formation of α -alkenes during the formation of active species at the contact of 1-hexene with the Re₂O₇/Al₂O₃ catalyst can be presented by the following scheme (Eq. 2–6).

$$Re^{n+} + CH_2 = CH(CH_2)_3CH_3$$

$$\rightarrow Re^* = CH_2 + CH_2 = CH(CH_2)_2CH_3$$
(2)

$$\begin{aligned} \operatorname{Re}^{n+} + \operatorname{CH}_2 &= \operatorname{CH}(\operatorname{CH}_2)\operatorname{2CH3} \to \operatorname{Re}^* \\ &= \operatorname{CH2} + \operatorname{CH}_2 = \operatorname{CHCH}_2\operatorname{CH}_3 \end{aligned} \tag{3}$$

$$2\operatorname{Re}^* = \operatorname{CH}_2 \to \operatorname{Re}^* + \operatorname{CH}_2 = \operatorname{CH}_2 \tag{4}$$

$$\begin{array}{rcl} \operatorname{Re}^* &=& \operatorname{CH}_2 \ + \ \operatorname{CH}_2 \ = \ \operatorname{CH}_2 \ - \ \operatorname{Re}^{n+} \ + \ \operatorname{CH}_2 \\ &=& \operatorname{CHCH}_3 \end{array} \tag{5}$$

$$Re^* = CH_2 + CH_2 = CHCH_3 \rightarrow Re^{n+} + CH_2$$

= CHCH_2CH_3 (6)

where Re^{n+} and Re^* stand for the precursor and active site, respectively.

 Table 3 Products of 1,1-D₂-1-hexene metathesis

Identified compound	Number of D atoms
Ethylene CD ₂ =CD ₂	4
Propene CD ₂ =CHCHD ₂	4
1,1-D ₂ -1-Pentene	2
1,1-D ₂ -1-Hexene	2
5-Decene	0

According to reaction (4), we may suppose that propene is formed as a result of the interaction of the methylidene fragment CH_2 of the carbene complex $Re^*=CH_2$ with ethylene playing the role of a scavenger for carbene. The results obtained in studying the metathesis of the deuterated alkene-1,1-dideutero-1-hexene are consistent with this idea (Table 3).

The formation of 1,1- D_2 -1-pentene can be explained by the occurrence of the reaction between the deuterated ethylene and 1-pentene formed during the metathesis of the starting 1,1- D_2 -1-hexene:

 $\begin{array}{rcl} CH_2 &=& CH(CH_2)_2CH_3 + & CD_2 = CD_2 \rightarrow CH_2 \\ &=& CD_2 + CD_2 = CH(CH_2)_2CH_3 \end{array}$

Furthermore, the addition of $CH_2=CD_2$ to the carbene complex Re*=D₂ accounts for the presence of deuterated propene CD₂=CHCHD₂ in the reaction products. The formation of propene and 1-butene during the conversion of 1-hexene on Re₂O₇/Al₂O₃ as the products of the interaction of ethylene and propene, respectively, with the active carbene complex Re*=CH₂ is also confirmed by the data obtained in studying the metathesis of terminal alkenes C₅--C₈ in the flow reactor (Table 4).

Indeed, it follows from Table 4 that the metathesis of all the alkenes C_5 - C_8 results in the formation of propene and 1-butene in the gas phase (and, to some extent, in the liquid phase), with the content of 1-butene being considerably higher in the case of the conversion of 1-pentene. This fact becomes understandable, since 1-butene in this case is the primary product formed at the first instant of the contact of 1-pentene with the activated catalyst surface, unlike the

Starting alkene	Time of reaction (min)	Composition of gas products (wt.%)			Composition of liquid products (wt.%)			
		Ethene	Propene	1-Butene	Main metathesis product	Side products ^a	Conversion	Selectivity to the main product (%)
1-Pentene	4-Octene							
	3	96.8	1.5	1.7				
	15	88.5	5.0	6.5	38.8	0.4	39.2	98
	60	87.6	5.7	6.7	38.6	Traces	38.6	100
1-Hexene	5-Decene							
	3	97.5	2.5					
	15	92.9	5.1	2.0	40.0	0.3	40.3	99
	60	92.7	5.0	2.3	44.6	0.5	45.1	99
1-Heptene	6-Dodecene							
	3	98.2	1.8					
	15	92.9	4.1	3.0	36.8	0.3	37.1	99
	60	93.3	3.9	2.8	34.6	0.6	35.2	98
1-Octene	7-Tetradecene							
	3	99.0	1.0					
	15	94.5	3.7	1.8	29.8	0.4	30.2	99
	60	94.5	3.5	2.0	32.3	0.7	33.0	98

Table 4 Composition of products formed in the conversion of α -alkenes C5–C8 (9 % Re/Al₂O₃, flow reactor, reaction temperature 200 °C, VHSV = 6 h⁻¹)

 $^{\rm a}$ The content of the 1-alkene having by one CH₂ group less than the starting alkene was 0.1–0.2 %

cases of the conversion of other α -alkenes. The formation of 1-butene as a result of the interaction of propene with Re^{*}=CH₂ is also consistent with the fact that 1-butene appears in the reaction products of the metathesis of alkenes C₆-C₈ at the later stages as compared with the appearance of propene (Table 4).

It should be noted that the migration of the double bond in the starting alkenes under the chosen conditions and on the chosen Re/alumina catalyst, unlike the case of silicaalumina-based metathesis catalysts [41–43], does not occur, and, hence, the formation of propene and 1-butene cannot be accounted for by the co-metathesis between the primary and secondary alkenes. Numerous experiments with 1-hexene metathesis showed that the alkene conversions at the initial instants of the contact with the catalyst and at the later stages of the development of the process are substantially different. This is explained by the consumption of 1-hexene in two different processes: the generation of the active species and the mere process of alkene metathesis.

The composition of the products formed from 1-hexene permanently changes with the time on stream (or residence time in the batch-wise experiments). These changes can be divided into two periods (Tables 2 and 5). It is seen from the data collected in these tables that, independently of the molar ratio alkene:Re, the 1-hexene conversion is low at the initial period (until 3–5 min). This is a so-called induction period of the reaction, which includes the formation of active sites of the metathesis reaction during the

first contact of the alkene with the activated catalyst $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$. This is supported by the predominant presence of α -alkenes in the reaction products: 1-pentene, 1-butene, and propene or even 1-pentene alone (Table 2).

During the second period of the process (after 3–5 min of time on stream), the composition of the products significantly changes: the percentage of α -alkenes, as a rule, decreases and higher alkenes with an internal double bond are formed (2-heptene, 3-octene, 4-nonene, 5-decene). The origin of the latter is obvious: they are the products of metathesis of the starting 1-hexene or co-metathesis of 1-hexene with the terminal alkenes formed at the stage of the generation of the active sites. The dynamics of accumulation and consumption of, for instance, 1-pentene and 4-nonene (Fig. 1) or propene and 1-butene (Fig. 2) under flow conditions confirm this hypothesis.

Finally, by the 30th min, only 5-decene in the liquid phase and ethylene in the gas phase can be found. In parallel, the selectivity to these two products increases by the end of the experimental run (Table 5). This is exactly the product composition reported in the numerous literature sources. However, these two products have little relation to the generation of the active sites. According to different estimates, the number of active sites in Re/alumina catalysts ranges from 0.03 to $\sim 3 \%$ of the total number of rhenium atoms in the catalyst [2, 27, 34]. We tried to make a similar estimate by assuming that the amount of 1-pentene formed at the very beginning stages of the interaction of 1-hexene

τ (min)	Composition of liquid products (wt.%) ^a								
	Propene	1-Butene	1-Pentene	2-Heptene	4-Nonene	5-Decene	Conversion ^b	Selectivity	
1	0.7	0.03	0.06	0.20	0.12		1.11		
3	0.7	0.07	0.07	0.31	0.22	16.7	18.7	89	
6	1.0	0.09	0.07	0.34	0.30	38.1	39.9	95	
10	1.2	0.12	0.07	0.32	0.29	47.9	49.9	96	
30	1.3	0.09	0.12	0.37	0.49	52.6	54.97	96	
45	1.3	0.05	0.08	0.41	0.60	56.0	58.44	96	
60	1.2	0.02	0.07	0.10	0.60	62.9	64.89	97	

Table 5 Variation of the product composition for 1-hexene conversion on Re_2O_7/Al_2O_3 (9 wt.% Re) at the molar ratio alkene: Re = 100:1, reaction temperature 20 °C, batch stirred reactor

^a Only ethylene and trace amounts of propene in the gas phase

^b 3-Octene was not detected in this experiment



Fig. 1 Variation of the yields of 1-pentene and 4-nonene as 1-hexene metathesis products on 9 wt.% Re/Al_2O_3 as a function of the conventional contact time under flow conditions

with the Re₂O₇/Al₂O₃ catalyst gives the number of the active sites (Table 2). The simple calculation gives the value of ~ 0.1 % of the total number of the Re ions in the catalyst. This finding is in close agreement with the data of the recent publication [37] showing that the total number of active sites on a MoO_x/SiO₂ catalyst does not exceed 1.5 % of the total number of molybdenum ions in the sample. The active Mo(VI)–alkylidene moieties, similarly to our case of the Recatalyst, are generated in situ by the surface reaction of grafted molybdenum oxide precursor species with the ole-finic substrate molecule.

4 Conclusions

Thus, the experimental proof of the formation of the carbene complexes at the surface of heterogeneous rhenium– alumina catalysts was obtained for the first time: the



Fig. 2 Variation of the yields of propene and 1-butene as 1-hexene conversion products on 9 wt.% Re/Al_2O_3 as a function of the conventional contact time under flow conditions

primary contact of the alkene substrate with Re₂O₇/Al₂O₃ results in the rupture of the C=C bond leading to the surface Re-carbene species containing the fragment of the alkene with a smaller molecular mass and to the alkene with the terminal C=C bond. So, 1-pentene is produced from 1-hexene. The schemes of the stages of the overall process were proposed based on the idea that alkenes with the terminal double bond are the primary products of the interaction of the starting alkene with the Re/alumina catalyst, whereas the alkenes with the internal double bond are the products of the metathesis of the starting alkene or cometathesis of this alkene with the primary products of the reaction. The further development of novel metathesis catalysts is related to the hybrid materials [44] and this topic will be addressed in our future research papers. The potential hybrid materials interesting for the application in metathesis include hierarchical structures (zeolites and the like) [33], Metal Organic Frameworks with supported Re

or Mo or solid supports with a supported layer of ionic liquid that contains Mo or Re species active in metathesis.

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References

- 1. Banks RL, Baily GC (1964) Ind Eng Chem Prod Res Dev 3:170
- 2. Ivin KJ, Mol JC (1997) Olefin Metathesis and Metathesis Polymerisation. Academic Press, New York
- 3. Grubbs RH, Wenzel AG, Chatterjee AK (2007) Comprehensive Organometallic Chemistry III. Elsevier, Amsterdam
- 4. Handbook of Metathesis, Ed. R.H. Grubbs (Wiley, New York, 2003)
- 5. Mol JC (2002) Green Chem 4:5
- 6. Mol JC (2004) J Mol Catal A 213:39
- 7. Sibeijn M, Spronk R, van Veen JAR, Mol JC (1991) Catal Lett 8:201
- 8. Wachs IE, Mol JC (1992) J Mol Catal 46:263
- 9. Edreva-Kardjieva RM, Andreev AA (1985) J Catal 94:97
- Schekler-Nahama F, Clause O, Commercuc D, Saussey J (1998) Appl Catal A 167:247
- 11. Danilyuk AF, Kuznetsov VL, Shmachkov VA, Kochubey DI, Chuvilin AL, Yermakov YuI (1988) J Mol Catal 46:209
- 12. Wang L, Hall WK (1983) J Catal 82:177
- Williams KPJ, Herrison J-L (1990) J Chem Soc, Faraday Trans 86:1603
- Vuurman MA, Stufkens DJ, Oskam A, Wachs IE (1992) J Mol Catal 76:263
- 15. Kerkhof FPJM, Moulijn JA, Thomas R (1979) J Catal 56:279
- 16. Xiaoding XU, Andreini A, Mol JC (1985) J Mol Catal 28:133
- 17. Nakamura R, Echigoya E (1982) J Mol Catal 15:147
- 18. Buffon R, Jannini MJDM, Abras A (1997) J Mol Catal A 115:173
- Nedez C, Lefebvre F, Choplin F, Basset J-M, Benazzi E (1994) J Am Chem Soc 116:3039

- 20. Xiexian G, Yide X, Yingzhen S, Yihua Z (1988) J Mol Catal 46:119
- 21. Yide X, Jiasheng H, Zhiying L, Xiexian G (1991) J Mol Catal 65:275
- 22. Moulijn JA, Mol JC (1988) J Mol Catal 46:1
- 23. Okal J, Kępinski L, Krajczyk L, Tylus W (2003) J Catal 219:362
- 24. Okal J, Tylus W, Kępinski L (2004) J Catal 225:498
- 25. Ellison A, Bickerstaffe A, Diakun G, Worthington P (1986) J Mol Catal 36:67
- 26. Ellison A, Diakun G, Worthington P (1988) J Mol Catal 46:131
- 27. Olsthoorn AA, Boelhouwer C (1976) J Catal 44:207
- 28. McCoy JR, Farona MF (1991) J Mol Catal 66:51
- 29. F. Kapteijn (1980) Ph. D. Thesis, University of Amsterdam
- 30. Kawai T, Goto H, Yamazaki Y, Ishikawa T (1988) J Mol Catal 46:157
- Tarasov AL, Shelimov BN, Kazansky VB, Mol JC (1997) J Mol Catal 115:219
- 32. G. Busca (2014) Heterogeneous Catalytic Materials
- 33. Balcar H, Čejka J (2013) Coord Chem Rev 257(21-22):3107
- 34. Sang L, Chen S-L, Yuan G, Zhou Z, Li R, Chen A, Zheng M, You J (2012) J Nat Gas Chem 21(3):352
- Skowerski K, Kasprzycki P, Bieniek M, Olszewski TK (2013) Tetrahedron 69(35):7408
- Bouchmella K, Stoyanova M, Rodemerck U, Debecker DP, Mutin PH (2015) Catal Commun 58:183
- Amakawa K, Wrabetz S, Kröhnert J, Tzolova-Müller G, Schlögl R, Trunschke A (2012) J Am Chem Soc 134:11462
- 38. Kustov LM (1997) Topics Catal 44:131
- 39. Makovetsky KL (1999) Neftekhimiya (Russ.) 39:379
- 40. Mol JC, Moulijn JA, Boelchouwer C (1968) Chem Commun 11:663
- Phongsawat W, Netiworaruksa B, Suriye K, Dokjampa S, Praserthdam P, Panpranot J (2012) J Nat Gas Chem 21(2):158
- Phongsawat W, Netiworaruksa B, Suriye K, Praserthdam P, Panpranot J (2014) J Ind Eng Chem 20(1):145
- Phongsawat W, Netiworaruksa B, Suriye K, Dokjampa S, Praserthdam P, Panpranot J (2012) J Nat Gas Chem 21(1):83
- Ananikov VP, Khokhlova EA, Egorov MP, Sakharov AM, Zlotin SG, Kucherov AV, Kustov LM, Gening ML, Nifantiev NE (2015) Mendeleev Commun 25:75