



International Conference on Oil and Gas Engineering, OGE-2015

Investigation of the Pt/MOR–Al₂O₃ catalysts by IR spectroscopy

Belopukhov E.A.^a * Paukshtis E.A.^b, Shkurenok V.A.^a, Smolikov M.D.^{a,c}, Belyi A.S.^{a,c}

^a*Institute of Hydrocarbons Processing SB RAS, 54, Neftezhavodskaya St., Omsk 644040, Russian Federation*

^b*Borekov Institute of Catalysis SB RAS, Lavrentieva Av. 5, Novosibirsk, 630090, Russian Federation*

^c*Omsk State Technical University, 11, Mira Pr., Omsk 644050, Russian Federation*

Abstract

Pt/MOR–Al₂O₃ catalysts, with platinum supported from H₂PtCl₆ and [Pt(NH₃)₄]Cl₂ solutions are investigated in the work with the methods of IR spectroscopy. The received results testify about platinum fixing mainly in channels of a mordenite in case of supporting from an ammine, and its localization on Al₂O₃ surface when supporting from chloroplatinic acid. Small concentration of the absorption bands referred to bridging CO species on platinum testify about high dispersion of metal on samples. Data explain higher activity of the catalysts prepared with [Pt(NH₃)₄]Cl₂ in reactions of a hydroisomerization of benzene and an isomerization of cyclohexane.

© 2015 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the Omsk State Technical University

Keywords: platinum; mordenite; alumina; FTIR CO and NH₃; DRIFT CO; cyclohexane; benzene; hydroisomerization

1. Introduction

Requirements to the quality of motor fuels of the vast majority of the countries to some extent limit the content of aromatic hydrocarbons and first of all benzene in automobile gasoline in connection with their high carcinogenicity [1]. One of perspective options of benzene removal from gasoline pool without loss of octane number is the process of a hydroisomerization of light benzol cut of a reformat at which benzene turns mainly in methylcyclopentane, and the accompanying paraffin hydrocarbons increase the depth of an isomerization. In the previous works as [2,3] the optimum composition of the catalyst representing the platinum supported on H-mordenite/alumina was chosen by the authors for this process. The purpose of this work – the research of catalysts by an IR spectroscopy method for

* Corresponding author. Tel.: +7-381-26-73-334.

E-mail address: eugebel@ihcp.ru

definition of acid characteristics of the support, and also localization and a charging condition of the platinum supported from H_2PtCl_6 and $[Pt(NH_3)_4]Cl_2$ solutions.

2. Experimental

2.1. Catalyst preparation

Supports and catalysts were prepared on described in [2] technique with the use of a mordenite (CBV 21A, Zeolyst International) with the SiO_2/Al_2O_3 ratio 20. $\gamma-Al_2O_3$ acted as the binder, received from a pseudoboehmite (Pural SB, Sasol Germany GmbH). The content of platinum in model samples is about 1.4 wt%. Designations, composition and some conditions of synthesis of the studied samples are presented in Table 1.

Table 1. Catalyst compositions and designations

Sample	Pt, wt%	Support composition	Pt precursor	T (air), °C	T (H ₂), °C
MOR	–	H-MOR – 100 %	–	500	–
AMOR	–	H-MOR – 30 % ; Al ₂ O ₃ – 70 %	–	500	–
Pt _{Am} /MOR	1.39	H-MOR – 100 %	$[Pt(NH_3)_4]Cl_2$	450	350
Pt _{Am} /AMOR	1.37	H-MOR – 30 % ; Al ₂ O ₃ – 70 %	$[Pt(NH_3)_4]Cl_2$	450	350
Pt _{Ac} /AMOR	1.39	H-MOR – 30 % ; Al ₂ O ₃ – 70 %	H_2PtCl_6	–	350
Pt _{Ac} /A	1.44	Al ₂ O ₃ – 100 %	H_2PtCl_6	–	350

2.2. IR spectroscopy

For registration of spectra, the samples were pressed without additional binder in tablets with a density of 15–20 mg/cm². The received tablets were vacuumized previously at 450 °C within 1 hour. Ammonia adsorption was carried out in the range of pressure of 0.1–10 torr at -190 °C. Adsorption of CO was carried out with a pressure interval of 10 torr and temperature of 100 °C within 10 minutes, then physically adsorbed ammonia was deleted with pumping out at 100 °C within 20 min. IR spectra were registered on Fourier Shimadzu 8300 spectrometer with the resolution of 4 cm⁻¹ and 100 scans for signal accumulation. The spectrometer is equipped with an DRS-8000 attachment of diffusion reflection. Spectra are presented after processing in a Origin software package. Error of measurements of concentration is ± 15 %.

3. Results and discussion

3.1. OH-groups

Spectra of hydroxyl groups of the samples vacuumized at a temperature of 450 °C are given in Fig. 1.

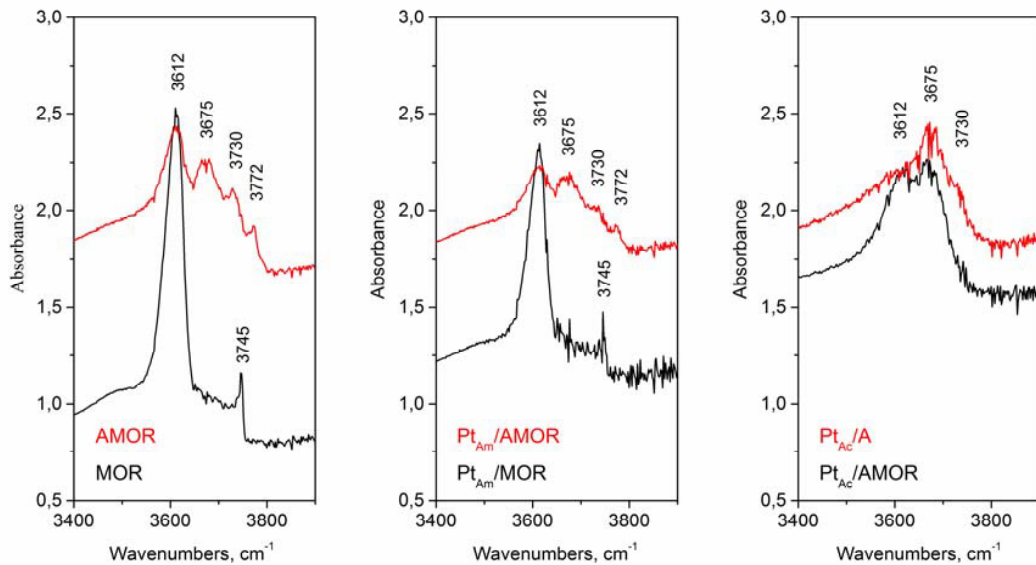


Fig. 1. Absorption spectra in the field of stretching vibrations of OH groups of the supports and catalysts vacuumized at 450 °C.

The absorption band at 3612 cm^{-1} which assigned to bridging hydroxyl groups Si-(OH)-Al responsible for Brønsted acidity of zeolites is observed on spectra of all studied mordenite samples. According to data [4] these OH groups are in channels of zeolites. The greatest intensity of the band 3612 cm^{-1} was observed, as it was expected, on MOR and Pt_{Am}/MOR samples, and the smallest one is on AMOR, Pt_{Am}/AMOR and Pt_{Ac}/AMOR composites. This fact shows the possibility of use alumina as the acidity regulator in composite supports.

IR spectra of MOR and Pt_{Am}/MOR samples except for the band 3612 cm^{-1} also contain an absorption band 3745 cm^{-1} which is characteristic for all zeolites and refers to terminal silanol group Si-(OH) [5–7]. Low intensity of the band 3745 cm^{-1} is connected with the low SiO₂/Al₂O₃ ratio of a mordenite. On the AMOR and Pt/AMOR samples where the content of zeolite is lowered to 30 wt%, the quantity of the silanol groups is also reduced, and the band is imperceptible.

The hydroxyl cover of γ -Al₂O₃ is characterized by three absorption bands: 3675, 3730 and 3772 cm^{-1} , assigned to two bridging Al^V-(OH)-Al^{IV}, Al^{VI}-(OH)-Al^{VI} and one terminal Al^V-(OH) hydroxyl groups, respectively [4,8].

When the catalyst prepared from H₂PtCl₆ solution (compare samples of AMOR Pt_{Ac}/AMOR, Pt_{Ac}/A, Figure 1) decrease in intensity of the band 3730 cm^{-1} , and also disappearance of the absorption band 3772 cm^{-1} is observed. That testifies that the process of fixing the platinum on the surface of alumina happens mainly with the help of the bridging hydroxyl groups connected with two octahedral coordinated cations of aluminum and a terminal hydroxyl group on a pentahedral coordinated aluminum cation. It is known that the Al^V-(OH) group qualitatively characterizes the deficiency of the alumina surface caused by effect of acid peptizer (acetic acid in our case). The platinum fixed in anion vacancies of defective structure is strongly kept by the support and often has an ionic form.

When fixing platinum on MOR and AMOR supports from the solution of ammonia [Pt(NH₃)₄]Cl₂ with the method of an ionic exchange the decrease in intensity of the absorption band 3612 cm^{-1} assigned to proton-donating bridging hydroxyl group Si-(OH)-Al is observed. Similar decrease in intensity can testify about fixing of platinum from an ammonia by means of this group located mainly in channels of zeolite.

3.2. CO adsorption

Spectral characteristics of the adsorbed CO are given in table 2. With low pressure CO is adsorbed on strong Lewis acid sites. With the pressure of 10 torr the molecule CO is adsorbed also on weak Lewis acid sites and on OH groups. Thus, changing CO pressure from 0.1 to 10 torr it is possible to allocate 4 types of Lewis acid sites (in Table 2 are provided in an order of increase in force).

Table 2. Position of absorption bands and concentration of the adsorbed CO on Lewis and Brønsted acid sites

Sample	Weak Lewis		Medium Lewis-1		Medium Lewis-2		Strong Lewis		Brønsted (CO – OH)	
	$\mu\text{mol/g}$	cm^{-1}	$\mu\text{mol/g}$	cm^{-1}	$\mu\text{mol/g}$	cm^{-1}	$\mu\text{mol/g}$	cm^{-1}	$\mu\text{mol/g}$	cm^{-1}
MOR	50	2198	–	–	33	2224	–	–	518	2173
AMOR	436	2187	8	2210	8	2222	02.03.15	2230	112 / 94	2175 / 2164
Pt _{Am} /MOR	280	2190–2200	–	–	70	2224	7	2230	384 / 200	2175 / 2164
Pt _{Am} /AMOR	380	2187–2200	51	2210	55	2224	15	2230	140 / 130	2176 / 2164
Pt _{Ac} /AMOR	435	2190	15	2210	5	2225	–	–	115 / 270	2176 / 2162
Pt _{Ac} /A	500	2190	30	2210	1	2224	–	–	108	2164

Observed for all samples with a pressure of 10 torr CO an intensive band in the field of 2160–2175 cm^{-1} is caused by formation of the CO complexes with acid OH groups. Thus the band 2164 cm^{-1} corresponds to weak Brønsted acid sites, and a band 2175 cm^{-1} – stronger. The band in the field of 2140 cm^{-1} assigned to physically adsorbed CO.

The spectral characteristics of catalysts connected with platinum are given in Table 3.

Table 3. The position of absorption bands of the CO complexes with platinum and quantity of CO connected with platinum

Sample	Pt ^{δ+}		Pt ⁰		Pt ⁰ (bridge)		Σ, μmol
	$\mu\text{mol/g}$	cm^{-1}	$\mu\text{mol/g}$	cm^{-1}	$\mu\text{mol/g}$	cm^{-1}	
Pt _{Am} /MOR	23	2122	2.7	2089	2.4	1890	28.1
Pt _{Am} /AMOR	15	2122	7	2099	–	–	22
Pt _{Ac} /AMOR	–	–	26	2093	–	–	26
Pt _{Ac} /A	–	–	24.3	2090	–	–	24.03.15

Absorption bands in area 2090 – 2100 cm^{-1} can be assigned to the linear CO complexes on Pt⁰, a band in the field of 2122 cm^{-1} – to the CO complexes on Pt^{δ+}, a wide absorption band in the field of 1890 cm^{-1} to the bridging CO complexes. The band 1890 cm^{-1} is observed only on Pt_{Am}/MOR sample. Low value of the concentration ratio of bridging CO to the sum of linear complexes (equal to 0.093) testifies about high dispersion of metal on the support.

3.3. DRIFT of adsorbed CO

IR spectra of the adsorbed CO after the evacuation at 25 and 200 °C are given in Figure 2.

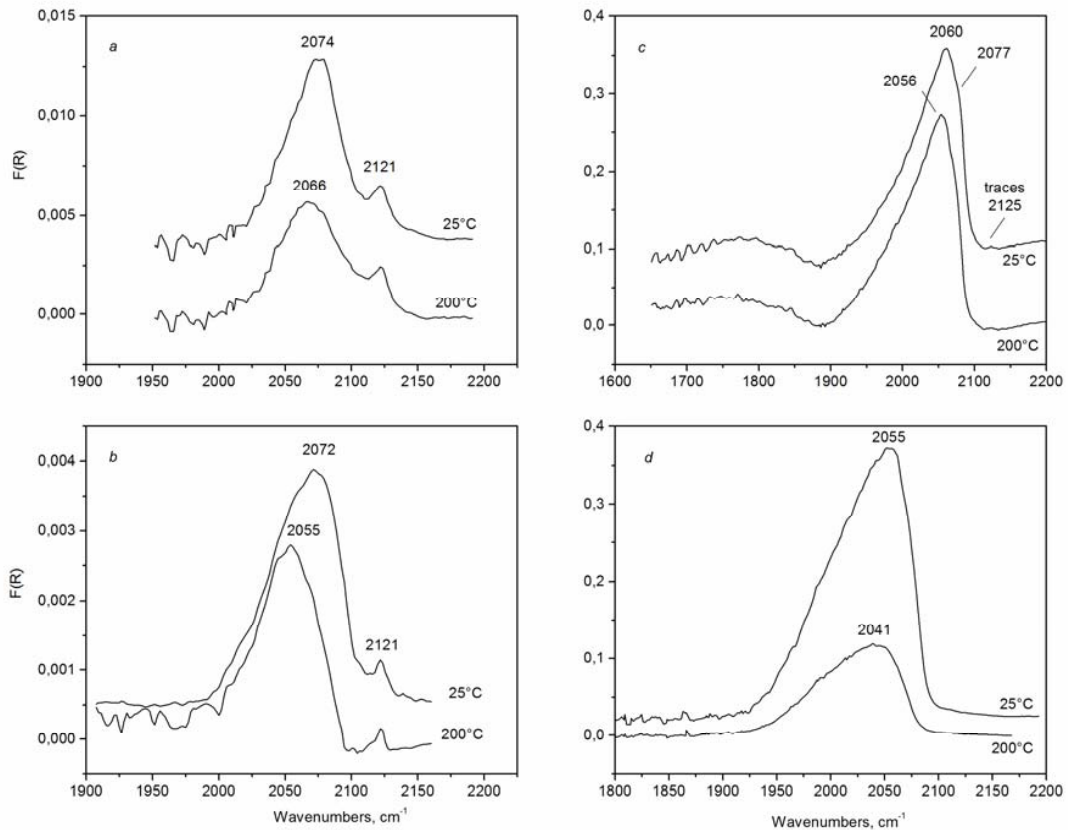


Fig. 2. FTIR spectra of CO adsorbed on Pt_{AM}/MOR (a), Pt_{AM}/AMOR (b), Pt_{Ac}/AMOR (c) and Pt_{Ac}/A (d), evacuated at the room temperature and at 200 °C.

FTIR spectra of adsorbed CO for the samples prepared with the use of [Pt(NH₃)₄]Cl₂ have a similar form with accurately expressed bands 2072 (2074) and 2121 cm⁻¹ assigned to the reduced (Pt⁰) and charged (Pt^{δ+}) platinum, respectively. In the same way the samples prepared with H₂PtCl₆ have the form similar among themselves. The intensive wide band 2055 (2060) cm⁻¹ assigned to the reduced platinum is characteristic for them. In the Pt_{Ac}/AMOR sample (Figure 3.c) except the band 2060 cm⁻¹ it is possible to see also the weakest band 2125 cm⁻¹.

Evacuating at high temperature leads to shift of bands of linear carbonyl complexes on 5–17 cm⁻¹ towards the reduction of wave number. Meanwhile the increase in temperature of evacuating doesn't affect the position of the band 2121 cm⁻¹ in any way (2125 cm⁻¹ – for Pt_{Ac}/AMOR sample). J.- K. Lee and H.- K. Rhee [9] consider that it is connected with small interactions between the adjacent molecules CO adsorbed on clusters of particles of Pt with electron-deficient structure (Pt–H)^{δ+}. Besides, according to J.-K. Lee these clusters are located in the channels of zeolite.

3.4. FTIR of adsorbed NH₃

Results of research of acidity by the IR spectroscopy of the adsorbed NH₃ are presented in Table 4.

Table 4. The position of the bands and concentration of the adsorbed ammonia on Brønsted and Lewis acid sites after desorption of 100 °C.

Sample	Brønsted		Lewis	
	$\mu\text{mol/g}$	cm^{-1}	$\mu\text{mol/g}$	cm^{-1}
MOR	1390	1447	27	1620
AMOR	397	1455	70	1620
Pt _{Am} /MOR	1240	1447	18	1620
Pt _{Am} /AMOR	336	1461	136	1620
Pt _{Ac} /AMOR	354	1454	167	1620
Pt _{Ac} /A	23	1470	282	1618

The absorption band 1450 cm^{-1} corresponds to the protonated form of ammonia NH_4^+ characterizing Brønsted acidity and the band 1620 cm^{-1} – to ammonia which coordinative bonded with the Lewis acid site. Absorption bands 1450 and 1620 cm^{-1} are present on spectra of all studied samples, thus it is obvious that Brønsted acidity is more typical for samples with the high content of zeolite, and Lewis acidity – for samples with the high content of alumina.

3.5. Catalytic investigation

Conversion of cyclohexane (CH) to methylcyclopentane (MCP) is the second stage of process of benzene hydroisomerization aimed at improvement of ecological parameters of automobile gasoline. Research of catalytic characteristics of samples with platinum (0.3 wt%) supported from H_2PtCl_6 and $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solutions, showed that most activity in reaction of an isomerization of cyclohexane shows the catalyst on the basis of an ammonia of platinum. Temperature dependences of cyclohexane conversion and selectivity of its transformation to methylcyclopentane are given in Figure 3.

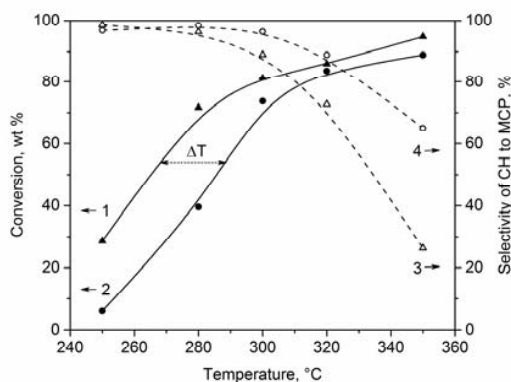


Fig. 3. Catalytic parameters of transformation of cyclohexane on Pt_{Am}/AMOR (▲ and △) и Pt_{Ac}/AMOR (● and ○). Conditions: P = 1.5 MPa, LHSV = 6 h⁻¹, H₂/CH = 3 mol/mol, catalyst volume of 2 cm³, fraction size of 0.2–0.7 mm.

It is visible that the activity of the Pt_{Am}/AMOR catalyst expressed by inverse function from temperature is 20 °C higher on average than activity of Pt_{Ac}/AMOR. Thus MCP yield at the level of 72–74 wt% on the catalyst from an ammonia platinum is reached at 300 °C, and on the catalyst from chloroplatinic acid – at 320 °C.

4. Conclusion

The results of research of Pt/MOR–Al₂O₃ system which active in benzene hydroisomerization reaction by methods of infrared spectroscopy adsorbed CO and NH₄ are presented in this work. It is shown that when supporting platinum from solution [Pt(NH₃)₄]Cl₂ the metal is both in the reduced condition Pt⁰, and in the charged condition Pt^{δ+}. According to the change of intensity of OH groups spectra when supporting platinum, and also the changing of position on of the adsorption bands assigned to the CO complexes with Pt^{δ+}, platinum is localized mainly in a porous matrix of a mordenite. When supporting platinum from solution H₂PtCl₆ the metal on the support is mainly in the reduced state, being localised on an alumina surface, and also on the defects of its structure, which formed due to decomposition of the acetic acid used at a peptization. Absence of the bands assigned with the bridging CO complexes on Pt (except for the sample of Pt_{Am}/MOR prepared on the supplier from a pure mordent), speaks about high dispersion of metal.

The obtained data explain higher activity of catalysts on the basis of [Pt(NH₃)₄]Cl₂ in comparison with prepared from H₂PtCl₆. So the most activity of the catalyst with platinum from an ammonia can be connected with direct proximity of the metal and acid sites, which participate in the bifunctional hydroisomerization mechanism, as platinum in this case is fixed on zeolite. When fixing platinum on Al₂O₃ the acid sites of zeolite are located further from metal, than in the first case therefore the transportation to them the intermediate complexes activated on platinum is complicated.

Acknowledgement

Authors express gratitude of Alexey B. Arbuzov for the help during the work on the article.

References

- [1] H. Bahadar, S. Mostafalou, M. Abdollahi, Current understandings and perspectives on non-cancer health effects of benzene: a global concern., *Toxicol. Appl. Pharmacol.* 276 (2014) 83–94.
- [2] E.A. Belopukhov, A.S. Belyi, M.D. Smolikov, D.I. Kir'yanov, T.I. Gulyaeva, Benzene hydroisomerization over Pt/MOR/Al₂O₃ catalysts, *Catal. Ind.* 4 (2012) 253–260.
- [3] E.A. Belopukhov, M.D. Smolikov, D.I. Kir'yanov, A.S. Belyi, The Effect of the Platinum Content on Pt/MOR/Al₂O₃ Activity in Benzene Hydroisomerization (in Russian), *Journal of Siberian Federal University. Chemistry.* 5 (2012) 398–404.
- [4] E.A. Paukshtis, *Infrared spectroscopy of heterogeneous acid-base catalysis* (in Russian), Nauka, Novosibirsk, 1992.
- [5] D.W. Breck, *Zeolite molecular sieves: structure, chemistry, and use*, John Wiley & Sons, New York, 1974.
- [6] C. Li, Z. Wu, *Microporous Materials Characterized by Vibrational Spectroscopies*, in: S. Auerbach, K. Carrado, P. Dutta (Eds.), *Handb. Zeolite Sci. Technol.*, CRC Press, New York, 2003.
- [7] V.B. Kazansky, L.M. Kustov, V.Y. Borovkov, Near infrared diffuse reflectance study of high silica containing zeolites, *Zeolites.* 3 (1983) 77–81.
- [8] O.B. Belskaya, I.G. Danilova, M.O. Kazakov, R.M. Mironenko, A.V. Lavrenov, V.A. Likholobov, FTIR Spectroscopy of Adsorbed Probe Molecules for Analyzing the Surface Properties of Supported Pt (Pd) Catalysts, in: T. Theophanides (Ed.), *Infrared Spectrosc. – Mater. Sci. Eng. Technol.*, InTech, 2012, pp. 149–178.
- [9] J.-K. Lee, H.-K. Rhee, Characteristics of Pt/H-beta and Pt/H-mordenite catalysts for the isomerization of n-hexane, *Catal. Today.* 38 (1997) 235–242.