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Gas Phase Study of *o*-Xylene Hydrogenation over Pt/Al_2O_3: The Influence of Ce and the Catalyst reduction Temperature on Selectivity

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In the hydrogenation of *o*-xylene, dispersion is affected by the reduction temperature. The activation energy (E_a^*) was found to be 67 ± 15 kJ/mol. The selectivity towards the thermodynamically preferred product, 1,2-*trans*-dimethyl cyclohexane isomer increases with the increase of dispersion, a behaviour explained by the roll over mechanism. The incorporation of Ce with Pt increases the percentage formation and the selectivity of the kinetically preferred product, 1,2-*cis*-dimethylcyclohexane isomer, and also it increases the activity of the hydrogenation. The effect of Ce was attributed to its electronic effect.

INTRODUCTION

The selectivity of *o*-xylene hydrogenation towards *cis*- and *trans*-isomers is reported to be affected by the type of metal, type and acidity of support, metal dispersity and carbonaceous residues. The selectivity is also affected by the catalyst preparation variables as metal precursor salt, solvent and catalyst reduction temperature.[1] It is reported that an increase of reaction temperature, metal dispersity and the acidity of the support lead to the increase of the selectivity towards the 1,2-*trans*-isomer,[2] while the decrease of the above variables and the use of electron-donor molecules favoured the 1,2-*cis*-isomer. A correlation between heat capacity of the metal conduction of electrons and the selectivity towards the 1,2-*cis*-isomer is also reported.[3]

Promotors were known to affect the activity and selectivity of a reaction due to their geometrical (particle size) effect and/or due to their electronic effect. Cerium was involved in this study on the fact that it acts as a catalytic promotor for many reactions.

This study was done to investigate the effect of changing dispersity as the reduction temperature of the catalyst changes and also the effect of incorporating Ce with the catalyst on the selectivity of the reaction.

EXPERIMENTAL

Flow system: The flow system which enables performing the dispersion and the catlytic activity measurements is shown in Fig. 1.

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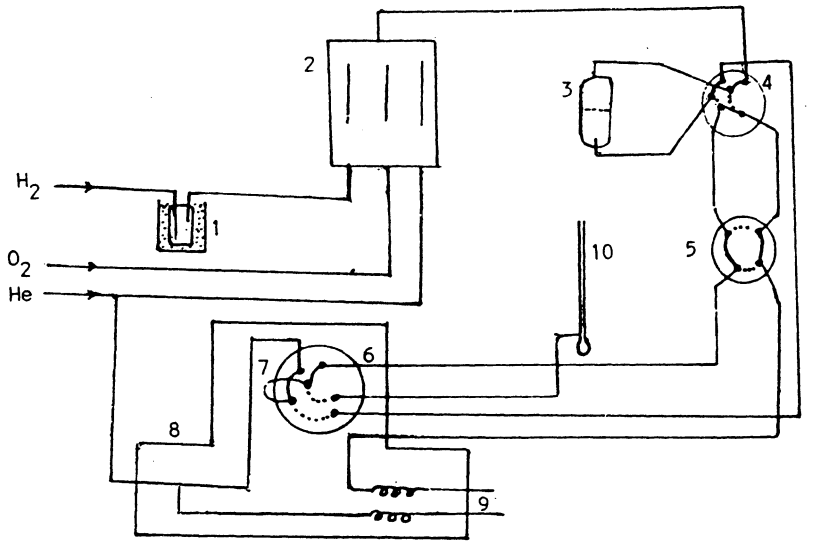

Fig. 1. Flow system: 1. Saturator, 2. Mass flow controller, 3. Reactor, 4. Six-port valve, 5. Four-port valve, 6. Sampling valve (six-port), 7. Sample loop, 8. Gas chromatograph, 9. Columns, 10. Flowmeter

Catalyst preparation: The Pt/Al_2O_3 catalyst used in this study was prepared by the incipient wetness technique. Initially, the appropriate weight of the $PtCl_4$ (Janssen Chimica, 99%) required to prepare a catalyst having a nominal weight loading of 1 w% Pt was dissolved in an amount of deionized water. The solution containing the Pt was added to the Al_2O_3 support (Merk, 150 m^2/g, high purity) in a dropwise manner to give a thick slurry. The resulting slurry was dried in air for 12 h at 120°C. Catalysts of different metal dispersity were obtained by varying the pretreatment reduction temperatures for four portions of the dried catalyst. The 1 w% Pt_{95}-Ce_5/Al_2O_3 was also prepared by the incipient wetness technique (co-impregnation method). The apropriate weights of $PtCl_4$ and ceric nitrate were dissolved in an amount of deionized water. The solution containing Pt and Ce was added to the alumina support in a dropwise manner to give a thick slurry. The resulting slurry was also dried in air for 12 h at 120°C.

Catalyst Pretreatment Schedules: Prior to the H_2 chemisorption measurements the catalyst portions were treated as follows: the catalyst samples were heated separately in flowing O_2 from 298 K to the assigned reduction temperature for 30 min followed by outgassing with He for 10 min. These samples were reduced by flowing H_2 for 3 h and then outgassed with He for 1 h; then they were cooled to room temperature while He was flowing and kept in vials for further use.

Chemisorption measurement: Dispersion for each catalyst was measured by using the pulse dynamic method.[4,5] Approximately 0.2 g of the pretreated sample was placed in the glass microreactor (6 mm id silica, 4.4 mL). The sample was heated to the assigned reduction temperature while He was flowing, then reduced in H_2 for 2 h, followed by flushing with He at the same temperature then cooled

to room temperature while He was flowing. The chemisorption was performed by pulsing H_2 into He carrier gas. The H_2 was detected by a thermal conductivity detector of Varian 3400 gas chromatograph connected to a Varian integrator model 4290.

Reaction: The hydrogenation reaction was performed in a continuous flow reactor at atmospheric pressure and at low conversion (20%) to avoid heat and mass transfer effects. The catalyst sample was put in the microreactor in a vertical furnace connected to a temperature controller and a thermocouple to control the temperature of the reactor. The catalyst sample was treated *in-situ* before starting the reaction. Hydrogen (756.3 torr) saturated with vapour of *o*-xylene (Fluka, 99.9%) at 14°C (3.7 torr) was passed through the reactor. The total gas flow rate of H_2 and *o*-xylene was 15 mL/min. This flow rate was controlled by using Matheson flow controller (multiple flow controller model 8274). The reaction products and the unreacted *o*-xylene were analysed by the gas chromatography with a column of 5% didecylphthalate plus 5% Benton on chromosorb W-Hp, 80/100, SST, 4-meter.

Between runs, when changing reaction temperature, the catalyst was maintained under pure hydrogen flow for at least 15 min. Under these reaction conditions only 1,2-*cis*-dimethylcyclohexane and 1,2-*trans*-dimethylcyclohexane isomers were obtained.

RESULTS AND DISCUSSION

The effect of the catalyst weight on the reaction selectivity was studied for the weights of 5 mg, 10 mg and 50 mg at a dispersion of 21% and a reaction temperature of 373 K (Table 1). The results show that selectivity is independent of the weight of the catalyst.

TABLE-1
EFFECT OF CHANGING THE CATALYST WEIGHT ON ACTIVITY AND SELECTIVITY OF *o*-XYLENE HYDROGENATION AT REACTION TEMPERATURE 373 K AND A DISPERSION OF 21% FOR Pt/Al_2O_3

Catalyst weight (mg)	% Conversion	Selectivity		TON × 10^3 molec. site^{-1} s^{-1}
		% *cis*	% *trans*	
5	20	79	21	0.19
10	45	79	21	0.31
50	100	80	20	0.54

The dispersion was calculated on the assumption of an H:Pt stoichiometry of 1:1. The turn-over number (TON) and the selectivity as a function of the reduction temperatures were listed in Table 2 at 373 K. The values of the activity and the selectivity were determined at the steady state (Fig. 2). The reaction rate measured for Pt/Al_2O_3 of different dispersions gave linear Arrhenius plots for the reaction temperature range of 323–373 K (Fig. 3). The average apparent activation energy was calculated from these plots and was found to be 67 ± 15 kJ/mol. This value

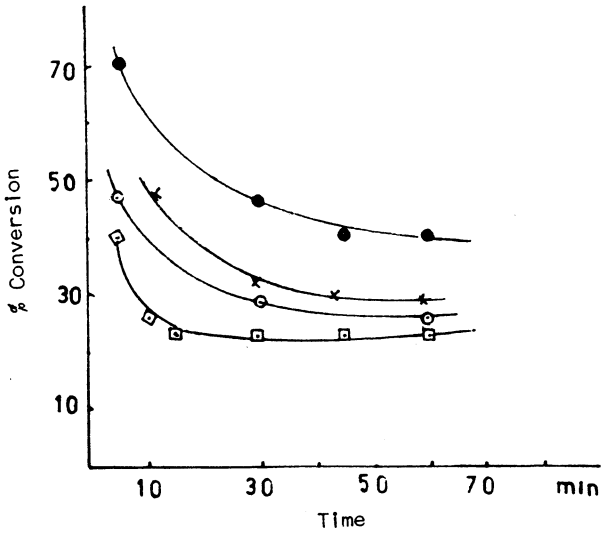

Fig. 2 Change of % conversion with time for *o*-xylene hydrogenation ever Pt/Al_2O_3
● Catalyst dispersion 33% ⊙ Catalyst dispersion 13%
× Catalyst dispersion 51% ⊡ Catalyst dispersion 21%

is comparable to that reported in the litrature.[6,7] The selectivity towards the 1,2-*cis*-isomer decreases with the increase of the reaction temperature (Fig. 4).

Since the increase of the reduction temperature causes a decrease in dispersion (Table-2), a sintering process must have taken place, which is responsible for the

TABLE-2
EFFECT OF THE REDUCTION TEMPERATURE ON DISPERSION AND SELECTIVITY FOR *o*-XYLENE HYDROGENATION OF REACTION TEMPERATURE 373 K AND 5 mg OF Pt/Al_2O_3

Reduction temperature (K)	% Dispersion	TON $\times 10^3$ molec. site^{-1} s^{-1}	Selectivity	
			% cis	*% trans*
623	51	0.11	75	25
673	33	0.27	77	23
723	21	0.19	79	21
773	13	0.40	80	20

formation of large metal particle size.[8] The results listed in this table and presented in Fig. 5 show clearly that the selectivity towards both isomers varies with dispersion. This implies that the formation of 1,2-*trans*-isomers increased with the increase of dispersion and implies that the formation of 1,2-*trans*-isomer is sensitive to metal particle size. A similar results were found by Del Angel *et al.*[9] and by Vinegra *et al*[10]. These authors changed the dispersity of the catalyst

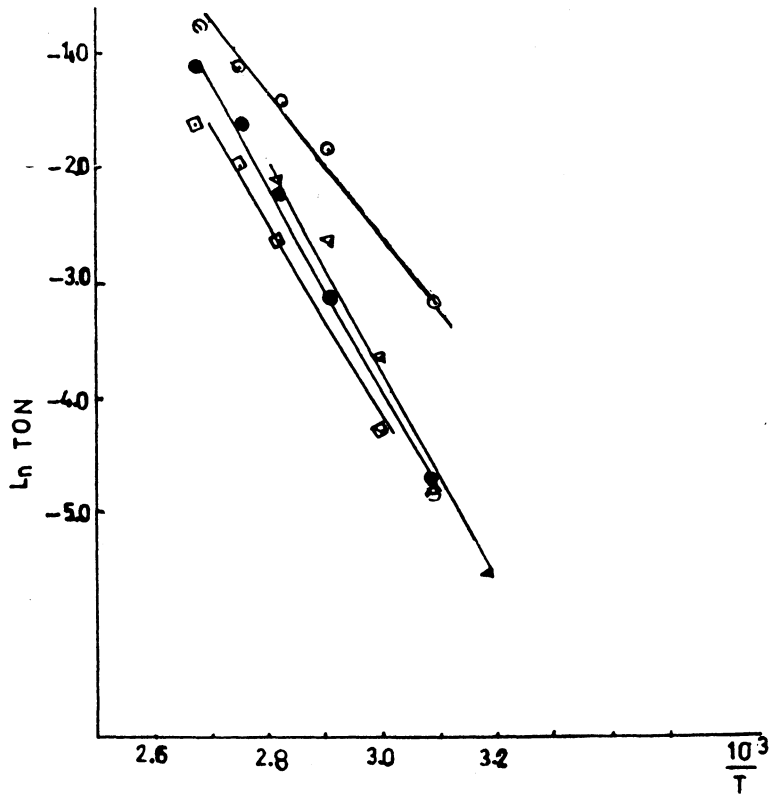

Fig. 3. Arrhenius plots for *o*-xylene hydrogenation over Pt/Al_2O_3
⊙ Catalyst dipersion 13% Δ Catalyst dispersion 21%
● Catalyst dispersion 33% ❑ Catalyst dispersion 51%

by using different supports. However, the change of the support assumes a change in the acidity of the reaction. Vinegra *et al.*[10] concluded that the selectivity depends on the acidity of the support. Therefore, the results obtained by varying the catalyst support do not define which factor is mainly affecting the selectivity the acidity or the metal particle size.

The formation of the *trans*-isomer can be explained by the desorption and readsorption of the 1,2-dimethylcyclohexene formed from the *cis*-addition. This mechanism demands the release of the olefin formed in the last step and then readsorption at the surface giving rise the *trans*-isomer. However, Hartog *et al.*[11] concluded from the kinetic analysis of the hydrogenation of benzene that only 1% of the hydrogenated benzene leaves the surface as cyclohexene and the remainder is hydrogenated during one sojourn on the surface. This led Siegel *et al.*[12] to propose that a different mechanism than the desorption and readsorption must be followed in order to explain the stereochemistry of *o*-xylene hydrogenation. Although the desorption and readsorption can explain the dependence of the selectivity of the *trans*-isomer with reaction temperature, it cannot justify the

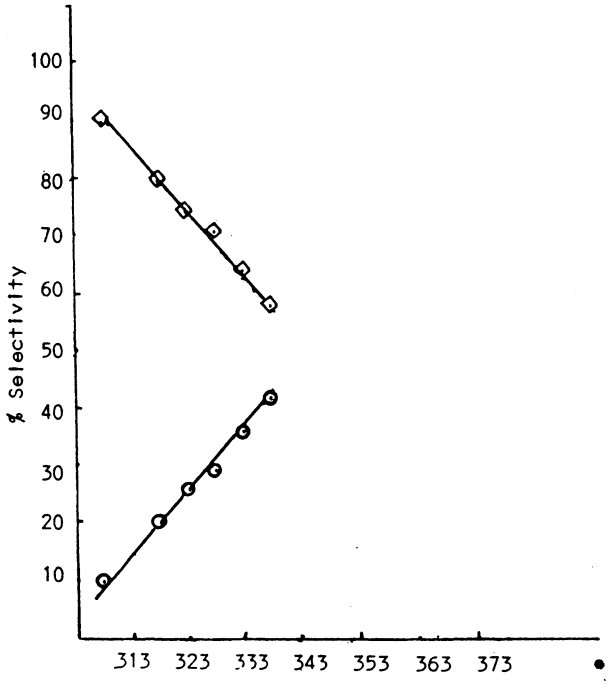

Fig. 4. Variation of selectivity toward *cis*- and *trans*-1,2-dimethylcyclohexane with temperature for *o*-xylene hydrogenation over Pt/Al_2O_3 of a dispersion 51%
❑ cis-1,2-dimethylyclohexane ○ *trans*-1,2-dimethylcyclohexane

dependence of the selectivity on dispersion. The selectivity dependence on dispersion can be explained by the roll-over mechanism, proposed by Inou *et al.*[13], in which the 1,2-*cis*-dimethylcyclohexene isomerizes to 2,3-dimethylcyclohexene, then by a roll-over process produces the 1,2-*trans*-isomer. Such a mechanism fits the situation where there is a large number of sites on the catalyst surface. Thus, the roll-over mechanism explains the observed dependence of the selectivity on dispersion.

The results listed in Table-3 and presented in Figs. 6 and 7 show that the incorporation of Ce in the Pt/Al_2O_3 catalyst has an effect on the reaction activity and selectivity. The presence of Ce increases the activity of the reaction. The reaction can be performed at such a low temperature as 303 K. The percentage formation of the 1,2-*cis*-isomer is higher over the Pt_{95}-Ce_5/Al_2O_3 catalyst compared to Pt/Al_2O_3 in the whole range of the temperature studied. This is reflected on the selectivity increase of the 1,2-*cis*-isomer over the Pt_{95}-Ce_5/Al_2O_3 catalyst (Table-3). The effect of Ce could be attributed to either an ensemble effect (geometrical) or to an electronic effect. However, the effect of Ce in the dispersion value is not large enough. The dispersion decrease from a value of 51% for the Pt/Al_2O_3 catalyst to a dispersion value of 47% for the

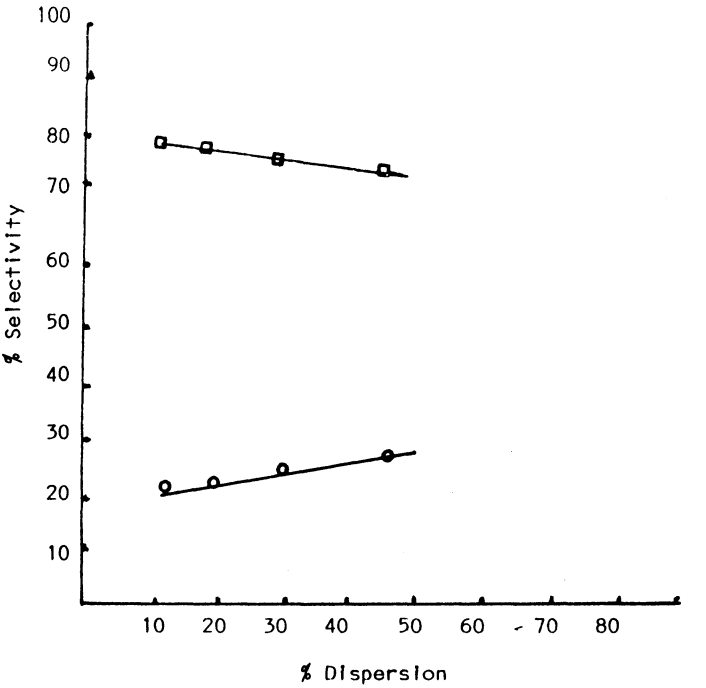

Fig. 5. Variation of selectivity towards *cis* and *trans* isomers with dispersion for the *o*-xylene hydrogenation over Pt/Al_2O_3

❑ *cis*-isomer o *trans*-isomer

Pt_{95}–Ce_5/Al_2O_3 (both catalysts are treated and reduced at the same reduction temperature). The results listed in Table-2 showed that a change in dispersion of *ca.* 38% causes an increase in the selectivity of about 5%, while a change in dispersion of *ca.* 4%, in case of the presence of Ce, causes a change in selectivity of about 2–4%, Table-3. This reveals that the increase of the selectivity and the increase of the pecentage formation of the *cis*-isomer, in case of Pt_{95}-Ce_5/Al_2O_3, is not mainly due to the ensemble effect (change of particle size). Vinegra *et al.*[1] studied the effect of injecting an electron donor species such as pyridine and thiophene to the reaction mixture. These authors found that the selectivity of the *cis*-isomer increases in the presence of these two electron donors. The electron donor molecule will increase the electron density of the metal active sites.

Since the *o*-xylene acts as a Lewis base towards the metal surface, this could lead to the conclusion that the stereoselectivity of the transition metal is determined by the time of residence of the *o*-xylene, and intermediate species on the surface, which in turn is determined by the bond strength. Therefore, the bond between the intermediate species and the metal is weak in the presence of an electron donor species. This will lead to the large formation of the kinetically preferred product which is the *cis*-isomer, while the formation of the thermodynamically preferred product, the *trans*-isomer, requires a longer residence time of the intermediate species in order that the roll-over process takes place.

TABLE 3
A COMPARISION BETWEEN Pt/Al_2O_3 AND Pt_{95}–Ce_5/Al_2O_3 ON THE SELECTIVITY AT DIFFERENT REACTION TEMPERATURES

Pt/Al_2O_3, Disp. = 51%,						Pt_{95}–Ce_5/Al_2O_3, Disp. = 47%				
Temp. (K)	% Conv. *o*-xylene	% F *cis-*	% F *trans-*	%S *cis-*	% S *trans-*	% Conv. *o*-xylene	% F *cis-*	% F *trans-*	% S *cis-*	% S *trans-*
303	0.0	0.0	0.0	0.0	0.0	2	2	0.0	100	0.0
313	0.0	0.0	0.0	0.0	0.0	5	4.5	0.5	90	10
338	16	16	0.0	100	0.0	25	21	4	84	16
353	30	23	7	76	24	48	38	10	80	20
373	60	48	15	75	25	70	54	16	77	23

% F = % Formation, % S = % Selectivity

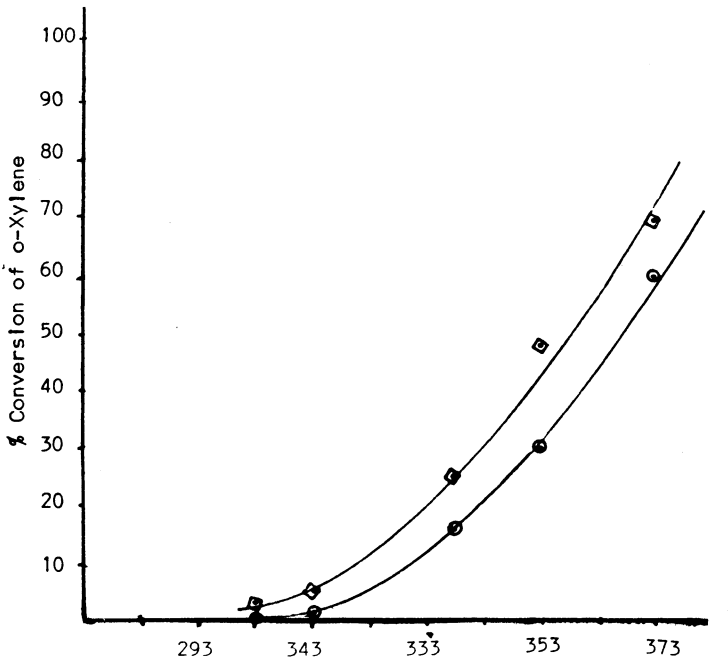

Fig. 6 A comparison between the % conversion of *o*-xylene over the catalysts
□ Pt_{95}-Ce_5/Al_2O_3 ⊙ Pt/Al_2O_3

According to the above explanation of an electron donor species and the observed selectivity results obtained over Pt_{95}-Ce_5/Al_2O_3 catalyst led us to conclude that Ce affects this hydrogenation reaction due to its electronic effect. This electronic effect of Ce has been observed in so many reactions. For example, the addition of Ce has been found to improve the thermal stability of alumina,[14] promote the reduction of supported metals and stabilize their reduced state.[15, 16]

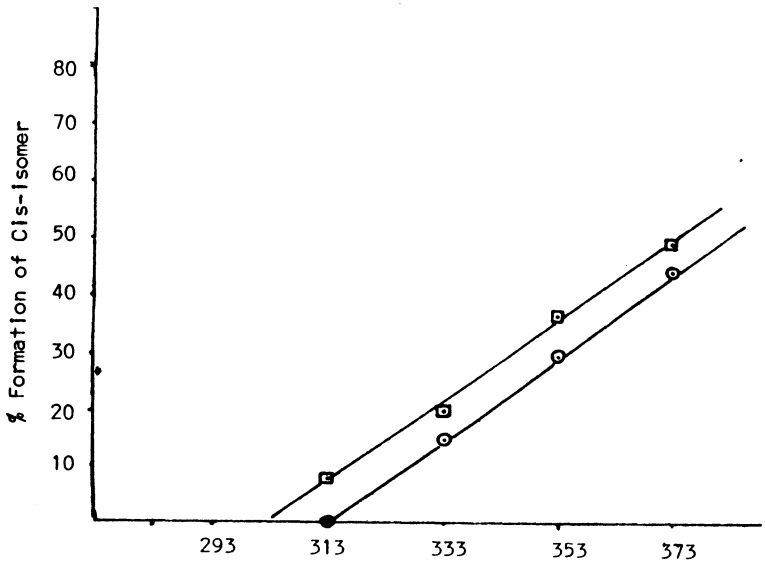

Fig. 7 A comparison between the % conversion of *o*-xylene over the catalysts
❑ Pt_{95}-Ce_5/Al_2O_3 ⊙ Pt/Al_2O_3

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REFERENCES

1. M. Viniegra, G. Cordoba and R. Gomez, *J. Molec. Catal.*, **58**, 107, (1990).
2. R. Gomez and O. Novaro, *React. Kinet. Catal. Lett.*, **45**, 251 (1991).
3. G. Del Angel, V. Bertin, A. Perez and R. Gomez, *React. Kinet. Catal. Lett.*, **48**, 259 (1992).
4. H.L. Gruber, *Anal. Chem.*, **34**, 1828 (1962).
5. J. Sarkany and R.D. Gonzalea, *J. Catal.*, **76**, 75 (1982).
6. M.V. Rahman and M.A. Vannice, *J. Catal.*, **127**, 251 (1991).
7. A. Stanislaus and B.H. Cooper, *Catal. Rev. Sci. Eng.*, **36**, 75 (1994).
8. J.R. Anderson, Structure of Metallic Catalysts, Academic Press, New York (1975).
9. R. Gomez, G. Del Angel and V. Bertin, *React. Kinet. Catal. Lett.*, **44**, 517 (1991).
10. M. Viniegra, N. Marin, A. Lopez-Gaona and G. Cordoba, *React. Kinet. Catal. Lett.*, **49**, 353 (1993).
11. F. Hartog and P. Zwietering, *J. Catal.*, **2**, 348 (1963).
12. S. Siegel, *Adv. Catal.*, **16**, 123 (1996).
13. Y. Inoue, J.M. Herrmann, H. Schmidt, R.L. Burwell, J.B. Butt and J.B. Cohen, *J. Catal.*, **53**, 401 (1978).
14. B. Harrison, A.T. Diwell and C. Hallet, *Platinum Met. Rev.*, **32**, 73 (1988).
15. J.C. Summers, and Al Ausen, *J. Catal.*, **58**, 131 (1979).
16. F. Le Norm, L. Hilaire, L. Killi, G. Krill and G. Maire, *J. Phys. Chem.*, **92**, 2561 (1988).

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